1990 Sampling Plan

Approved 10-26-90

FILE COPY

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
REGION 5
230 SOUTH DEARBORN ST.
CHICAGO, ILLINOIS 60604

REPLY TO ATTENTION OF: 5SMQA

MEMORANDUM

DATE: OCT 26 1990

SUBJECT: Approval of PRP-Lead Quality Assurance Project Plan for Sampling and Analysis of Groundwater and Granular Activated Carbon Treatment System - As part of the Remedial Investigation/Feasibility Study Activity at the Reilly Tar and Chemical Corporation Site in St. Louis Park, Minnesota

FROM: Valerie J. Jones
Regional Quality Assurance Manager

TO: John Kelley, Acting Chief
Remedial and Enforcement Response Branch (5HS)

ATTENTION: Darryl Owens, Remedial Project Manager

I am providing approval of the second revision, PRP-Lead Quality Assurance Project Plan (QAPjP) for sampling and analysis of groundwater and granular activated treatment system - as part of the Remedial Investigation/ Feasibility Study (RI/FS) activities at the Reilly Tar and Chemical Co. site in St. Louis Park, Minnesota. This subject QAPjP was received by the Quality Assurance Section (QAS) on October 23, 1990 (QAS Log-In No. 1381).

The signed original signature page is included. Please have the Remedial Project Manager provide final sign off. Please send us a copy of the completed signature when it is available.

Attachment

cc: Kaushal Khanna, TSU

QUALITY ASSURANCE PROJECT PLAN
FOR SAMPLING AND ANALYSIS - GROUNDWATER
AND GAC PLANT MONITORING

Prepared by

The City of St. Louis Park
St. Louis Park, MN 55416

Approved by ______________________ Date: ______________
Gary Torf, Quality Assurance
Director, Rocky Mountain Analytical Laboratory

Approved by ______________________ Date: ______________
James N. Grube, Project Manager
City of St. Louis Park, MN

Approved by: Dale A. Goss Date: Oct. 26, 1990
Quality Assurance Officer
U.S. EPA Region V

Approved by: ______________________ Date: ______________
Remedial Project Manager
U.S. EPA Region V

Approved 10-26-90
Includes Rev 0
~~Sampling Plan~~
Site Management
Plan + Rev 1 QAPP
+ Rev 2 QAPP Revised
pages

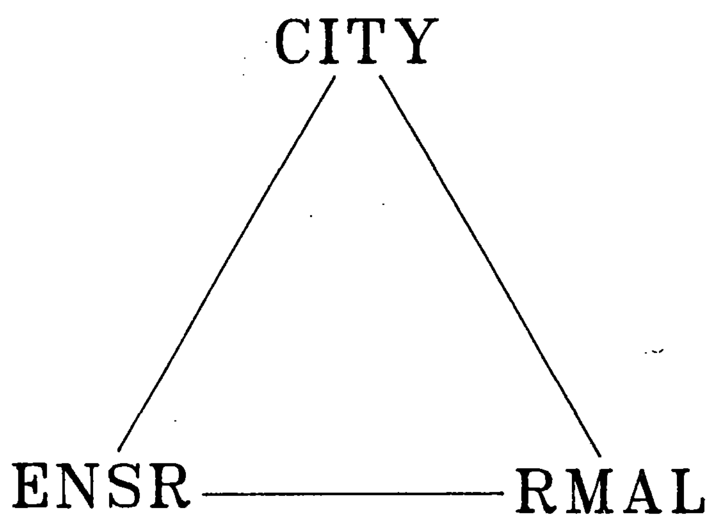
QUALITY ASSURANCE BRANCH

NOV 16 1989

ENVIRONMENT SERVICES DIVISION

SAMPLING PLAN FOR REILLY TAR & CHEMICAL CORP. N.P.L. SITE ST. LOUIS PARK, MINNESOTA

SUBMITTED OCTOBER 31, 1989



SITE MANAGEMENT PLAN

INTRODUCTION

Ground water in the City of St. Louis Park, Minnesota has been found to contain polynuclear aromatic hydrocarbons (PAH) and phenolics as a result of activities at a coal-tar distillation and wood preserving plant (Site) operated from 1917 to 1972. Numerous previous studies have identified PAH's in various aquifers beneath St. Louis Park and adjacent communities.

The United States Environmental Protection Agency (EPA), the Minnesota Pollution Control Agency (MPCA), the Minnesota Department of Health (MDH), the City of St. Louis Park (City), and Reilly Industries, Inc. (formerly Reilly Tar & Chemical Corporation - Reilly) have agreed to acceptable water quality criteria for PAH. These criteria, as incorporated into a Consent Decree, include the following concentration levels:

	Advisory Level	Drinking Water Criteria
o Sum of benzo(a) pyrene and dibenz(a,h) anthracene	3.0 ng/l*	5.6 ng/l
o Carcinogenic PAH	15 ng/l	28 ng/l
o Other PAH	175 ng/l	280 ng/l

* or the lowest concentration that can be quantified, whichever is greater

In conjunction with the implementation of remedial measures to limit the spread of PAH and phenolics, a granular activated carbon (GAC) treatment system has been installed to treat water from City wells (identified - SLP) 10 and 15. Further provisions of a Remedial Action Plan (RAP) call for long-term monitoring of the influent and effluent of the GAC treatment system and the major aquifers underlying the region. The general objective of the monitoring program is to identify the distribution of PAH and/or phenolics in the ground water. The analytical data will be used to evaluate water quality by comparing the levels of PAH and/or phenolics found in the various samples with historical water quality data and with water quality criteria established in the Consent Decree-RAP. The specific objectives of the monitoring program, and therefore, the intended end use of the data vary slightly for the different aquifers being monitored in accordance with the Consent Decree-RAP.

The objective of the GAC treatment system monitoring is to assess and evaluate the performance of the treatment system. Analytical results for influent and effluent samples will be compared to the drinking water criteria for PAH as established in the Consent Decree-RAP. Based on these comparisons, decisions will be made on: 1) system operations (e.g., when the carbon should be replaced), and 2) cessation of the treatment system, if desired, when sufficiently low concentrations of PAH in influent samples are demonstrated.

The objective of monitoring the four existing Mt. Simon-Hinckley Aquifer municipal drinking water wells and any new Mt. Simon-Hinckley Aquifer municipal drinking water wells installed within one mile of well W23, and analyzing for PAH, is to assure the continued protection of these wells from PAH resulting from activities of Reilly at the Site. The analytical data will be used to make comparisons between the levels of PAH found in the Mt. Simon-Hinckley Aquifer, and the drinking water criteria established in the Consent Decree-RAP.

The objective of monitoring the Ironton-Galesville Aquifer source control well (W105) is to assess the levels of PAH in the discharge from W105 when it is pumping a monthly average of 25 gallons per minute. The data will be used to compare the concentration of total PAH in the samples to a cessation criterion of 10 micrograms per liter of total PAH established in the Consent Decree-RAP. In the event monitoring results indicate the water quality has improved to within cessation criterion, the City will petition the EPA and MPCA for authorization to discontinue the pumping of W105. Also, if any new Ironton-Galesville Aquifer drinking water wells are installed within one mile of well W23, then those wells will be sampled and analyzed for PAH to meet the objective of assuring protection of the wells from PAH resulting from the activities of Reilly at the Site. The analytical data will be used to compare the levels of PAH found in potential Ironton-Galesville Aquifer drinking water wells to the drinking water criteria established in the Consent Decree-RAP.

The objectives of monitoring the many Prairie du Chien-Jordan Aquifer wells, including municipal drinking wells, private or industrial wells, and monitoring wells are to: 1) monitor the distribution of PAH in the aquifer, thus evaluating the source and gradient control systems, and 2) assure the continued protection of drinking water wells from PAH resulting from the activities of Reilly at the Site. The analytical data will be used to compare the levels of PAH in the Prairie du Chien-Jordan Aquifer to historical PAH data and to various criteria established in the Consent Decree-RAP (e.g., drinking water criteria for drinking water wells, and a cessation criterion of 10 micrograms per liter of total PAH for source control well W23). Water level data will be used to evaluate ground water flow patterns in the Prairie du Chien-Jordan Aquifer.

The objectives of monitoring St. Peter Aquifer wells are to: 1) monitor the distribution of PAH in the aquifer, thus evaluating a gradient control system installed at W410 in 1990, and 2) assure the continued protection of drinking water wells from PAH resulting from the activities of Reilly at the Site. The analytical data will be used to compare the levels of PAH in the St. Peter Aquifer to historical PAH data, to drinking water cessation criteria for well W410, and to drinking water criteria established in the Consent Decree-RAP. Water level data will be used to evaluate ground water patterns in the St. Peter Aquifer.

The objective of monitoring the Drift-Platteville Aquifer wells is to monitor the distribution of PAH and phenolics in the aquifer, thus evaluating the source and gradient control systems. The analytical data will be used to compare levels of PAH and phenolics in the Drift- Platteville Aquifer with historical water quality data for the aquifer and with various criteria established in the Consent Decree-RAP for PAH and phenolics. Water level data will be used to evaluate ground water flow patterns in the Drift-Platteville Aquifer.

The Site Management Plan outlines the scope of work to be performed in order to monitor the ground water in the St. Louis Park, Minnesota area in accordance with the Consent Decree-RAP related to the Reilly Tar & Chemical Corporation N.P.L. Site. Included in this plan are: 1) the identity of wells to be monitored, 2) the schedule for ground water monitoring, and 3) a description of the procedures that will be used for sample collection, water level measurement, sample handling, sample analysis, and reporting.

The time period covered by this Plan is from January 1, 1990, or the date of its acceptance and approval by the Agencies whichever is later, to December 31, 1990. The next subsequent Sampling Plan (RAP Section 3.3) will be submitted by October 31, 1990 covering the 1991 calendar year.

This Plan incorporates the requirements of RAP Sections 3.2, 3.3, 4.3, 5.1, 6.1.4, 7.3, 8.1.3, 9.1.3, 9.2.3, 9.3.3, and 9.6. Some of the monitoring required under these RAP Sections has already taken place in accordance with previous Sampling Plans.

MONITORING SCHEDULE

The monitoring schedule outlined in this Plan indicates the starting criteria and the frequencies of monitoring as outlined in the RAP to determine when the wells are monitored (Tables 1 and 2). In general, the monitoring schedule will allow economies of scale in the field and in the laboratory by grouping the various monitoring events described by the RAP as much as possible. Samples will be collected within the time periods indicated on Tables 1 and 2, and all parties will be given at least 48 hours notice in advance of routine sampling.

Tables 1 and 2 summarize the GAC system ground water monitoring schedule for the period through December 1990, and represent the minimum monitoring program that is likely to occur during the year. However, additional monitoring will take place if treated water from the GAC treatment system or ground water from active municipal drinking water wells exceeds the drinking water criteria established in the Consent Decree-RAP. This additional monitoring is described in Sections 4 and 12 of the RAP, and are reproduced in Appendix A of this Site Management Plan.

The duration of field sampling events will depend on the number and type of wells to be monitored. For estimating purposes, Drift-Platteville Aquifer monitoring wells typically are monitored at a rate of 10 wells per day, St. Peter Aquifer monitoring wells typically monitored at a rate of 6 wells per day, and Prairie du Chien Aquifer monitoring wells typically require two to four hours or more per well to monitor.

TABLE 1

SAMPLING PLAN GAC TREATMENT SYSTEM MONITORING SCHEDULE [(a)]

RAP Section	Sampling Points	Start of Monitoring	Sampling Frequency	Analyses[(b)]
4.3.1(C)	Treated water (TRTD)	Date of plan approval	Quarterly	PAH(ppt)[(c)]
4.3.3(C)	Feed water (FEED)	Date of plan approval	Annually	PAH(ppt)
4.3.4	Treated water	Date of plan approval	Annually	Extended PAH(ppt)
4.3.4	Treated or Feed water	Date of plan approval	Annually	Acid fraction compounds in EPA Test Method 625.

(a) This schedule does not include certain contingencies (e.g. exceedance monitoring) and, therefore, represents the minimum program that is likely to occur between the date this Plan is approved and December 31, 1990. Sections 4 and 12 of the RAP outline the additional monitoring that will be conducted if PAH criteria are exceeded. The first samples will be collected during the period indicated by the monitoring frequency following the date of the start of monitoring. The location of the GAC treatment system is shown in Figure 1.

(b) Lists of parameters and methods for analysis of PAH, extended PAH, and acid fraction compounds in EPA Test Method 625 are provided in the QAPP. Field blanks will be collected and analyzed at a frequency of one per day. Duplicate samples will be collected and analyzed at a frequency of one per 10 samples.

(c) ppt = parts per trillion. This signifies analysis using selected ion monitoring gas chromatography mass spectrometry.

REVISED
Oct., 1990

TABLE 2
SAMPLING PLAN GROUND WATER MONITORING SCHEDULE [a]

Source of Water	RAP Section	Sampling Points[b]	Start of Monitoring	Sampling Frequency	Analyses[c]
Mt. Simon-Hinckley Aquifer	5.1	SLP11,SLP12, SLP13,SLP17	Date of plan approval	Annually	PAH(ppt)[d]
	5.3.2	New municipal wells within one mile of well W23	At the time of installation	Annually	PAH(ppt)
Ironton-Galesville Aquifer	6.1.4	W105 W38[e]	Date of plan approval	Quarterly	PAH(ppt)
	6.2.1	New municipal wells within one mile of well W23	At the time of installation	Annually	PAH(ppt)
Prairie du Chien-Jordan Aquifer	7.3(A)[f]	SLP4	Start of pumping	Quarterly	PAH(ppt) phenolics
	7.3(B)[f]	W23	Date of plan approval	Semi-annually	PAH(ppb)[g]
	7.3(C)[f]	SLP6,SLP7 or SLP9,W48	Date of plan approval	Quarterly	PAH(ppt)
	7.3(D)[f]	W405 or W406[h] E2,E13,H3, SLP10 or SLP15, SLP14,SLP16,W402 W403,W119	Date of plan approval	Semi-annually	PAH(ppt)
	7.3(E)[f]	SLP5,H6,E3, E15,MTK6, W29,W40, W70,W401	Date of plan approval	Annually	PAH(ppt)
	7.3(F)	W32,SLP8, SLP10,E4, E7	Date of plan approval	Quarterly	No Chemical analyses[i]
St. Peter Aquifer	8.1.3	SLP3,W11,W33, W129,W133, W408,W409	Date of plan approval	Semi-annually	PAH(ppt)

TABLE 2 (continued)

Source of Water	RAP Section	Sampling(b) Points	Start of Monitoring	Sampling Frequency	Analyses(c)
Drift-Platteville Aquifer	9.1.3 and 9.2.3	W420,W421, W422	Date of plan approval	Quarterly	PAH(ppb) and total phenols
	9.6	Drift:W10, W15,W116,W117, W128,W423,W427, P109,P112,P306, Platteville: W20,W22,W101, W121,W124,W130, W132,W424, W428,W430	Date of plan approval	Annually(j)	PAH(ppb/ppt) and total phenols

(a) This schedule does not include certain contingencies (e.g. exceedance monitoring) and, therefore, represents the minimum program that is likely to occur between the date this Plan is approved and December 31, 1990. Section 12 of the RAP outlines the additional sampling that will be conducted if the drinking water criteria are exceeded in samples from water supply wells. The first samples will be collected during the period indicated by the monitoring frequency following the date of the start of monitoring. Field blanks will be collected at a frequency of one for every 10 samples or fewer, and one duplicate sample will be collected for every 10 samples.

(b) Sampling points are located on the maps shown in Figures 1 through 5. Letter prefixes to well codes are defined as follows:

W - 4-inch monitoring well

P - monitoring piezometer

SLP - St. Louis Park supply well

E - Edina supply well

H - Hopkins supply well

MTK - Minnetonka supply well

TABLE 2 (continued)

(c) Lists of parameters and descriptions of the methods for analysis of PAH, phenolics, and expanded analyses are provided in the QAPP. Water levels will be measured each time samples are collected for analysis, except for those wells which prove to be inaccessible for such measurements.

(d) ppt = parts per trillion. This signifies analysis using selected ion monitoring gas chromatography mass spectrometry.

(e) Water levels in W38 will be measured each time W105 is sampled.

(f) Water level measurements will be made quarterly at these wells, except for those wells which prove to be inaccessible for such measurements.

(g) ppb = parts per billion. This signifies analysis by the Non-Criteria Method. If analytical results for individual wells are below 20 micrograms per liter (20 ppb) using this method, then the Low-Level Method will be used on subsequent monitoring rounds.

(h) W405 = American Hardware Mutual, W406 = Minikahda Golf Course.

(i) Water levels only (no monitoring) will be measured at these wells, except for those wells which prove to be inaccessible for such measurements. (NOTE: W112 has been properly abandoned and will no longer be included in this or subsequent Plans.)

(j) If any of the wells listed here become damaged, destroyed, or otherwise unsuitable for sampling, alternate wells will be selected by the Project Leaders for monitoring.

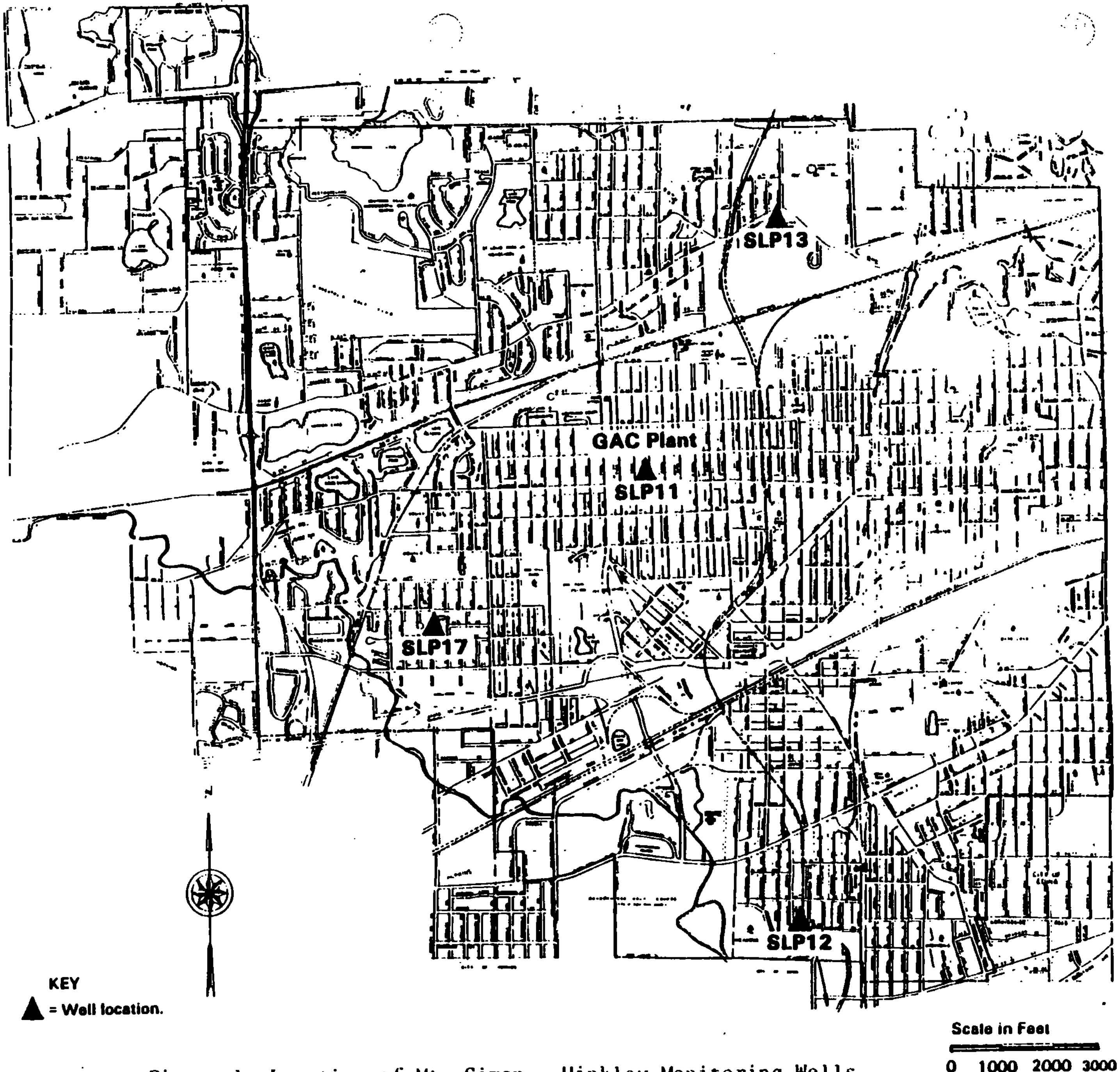


Figure 1 Location of Mt. Simon - Hinkley Monitoring Wells and St. Louis Park GAC Water-treatment Plant

[redacted]

Figure 2 Location of Praire du Chien-Jordan Aquifer Wells

[redacted]

NON-RESPONSIVE

Figure 3 Location of Source and Gradient Control Wells

NON-RESPONSIVE

[redacted]

0 500 1000 2000
FEET

N

EXPLANATION

● DRIFT WELLS

■ PLATTEVILLE WELLS

Figure 4 Location of Drift-Platteville Monitoring Wells

Reference: MGS, Miscellaneous Map Series,
M-57, Plate 1 of 2, Bedrock Geology,
[redacted]

NON-RESPONSIVE

EXPLANATION

▲W 33 LOCATION AND PROJECT WELL NUMBER

▲ OBSERVATION WELL COMPLETED IN ST. PETER AQUIFER

■ OBSERVATION WELL COMPLETED IN BASAL ST. PETER CONFINING BED

⊙ ST. PETER AQUIFER CONTROL WALL W410

BEDROCK VALLEY/CONTACT WHERE UNCONSOLIDATED DRIFT
DEPOSITS OVERLIE ST. PETER SANDSTONE

Figure 5 Existing St. Peter Aquifer Well Locations and Bedrock Valley

GROUND WATER SAMPLING PROCEDURES

An important distinction is made between the sampling procedures for active pumping wells (e.g. municipal wells) and for non-pumping monitoring wells. Active pumping wells are used on a regular basis, have dedicated pumps and associated plumbing, and have sample taps for collecting samples. Non-pumping monitoring wells may be new, or may have not been pumped for several years, and most require pumping and associated equipment for sampling. Another distinction is that the active pumping monitoring wells are typically located inside buildings whereas monitoring wells are not.

With these considerations in mind, this Plan has been developed so that the ground water monitoring program in each aquifer meets the requirements and intent of the RAP. Ground water monitoring will be conducted in accordance with the procedures given in the Quality Assurance Project Plan (QAPP), and with "Procedures for Ground Water Monitoring: Minnesota Pollution Control Agency Guidelines", April 1985.

Water Level Measurements

Water level measurements will be made using electric tapes or weighted steel tapes. Water level measurements using steel tapes will be made by suspending a known length of tape in the well so that the bottom end of the tape is below the water level. The lower portion of tape will be coated with blue chalk that exhibits a noticeable color change when wetted. The water level measurement will be obtained by subtracting the length of wetted tape from the total length of tape suspended below the measuring point of each well.

Using the electric tape, the probe at the end of the tape will be lowered slowly in the well until contact with the water is made. Because of surface tension, readings of the water level made when the probe enters the water will differ from readings made when the probe leaves the water, thus breaking surface tension. To standardize these measurements, the second reading will always be used (i.e., the reading made when the probe leaves the water).

Water level measurement made for the purpose of defining ground water flow patterns in a particular aquifer will be performed independently from groundwater sampling, as a discrete event (probably lasting one or two days). The wells will be revisited for sampling, and measurements to determine the volume of water in the well will be made at that time.

Sample Collection at Active Pumping Wells

At active pumping wells the sampling team will first determine that the wells have actually been pumping during the period preceding sampling. This information may be derived from inspecting flow recorders or from interviewing knowledgeable persons regarding the wells (water department employees, well owners, etc.). The information will be documented in the field notes of the sampling team.

Water level measurements will then be made, if practical. The normal operation of the well will not be interrupted for the purpose of measuring water levels. An electric tape will be used to measure water levels in pumping wells. Sampling will proceed by filling the required containers with water from the sampling tap as near to the well head as possible, and before any holding tanks or treatment is encountered. The only exception to this is the GAC treatment system monitoring under RAP Section 4.3 which includes treated water monitoring.

If it can not be determined that a well has been pumping at some time during the 24 hour period preceding sampling, or if it is known the well was not pumping, then the well shall be purged until field measurements of temperature, pH, and specific conductance have stabilized after at least three well volumes have been removed from the well. These measurements, water levels, and the amount of water pumped will be recorded in the field notes.

Sample Collection at Monitoring Wells and Piezometers

Because unanticipated or changed conditions may cause difficulty in the purging and sampling of the monitoring wells and piezometers, flexibility in the approach to sample retrieval is necessary. This Plan proposes that the sampling team be given latitude in the selection of purge/sample equipment and procedures necessary to compete the monitoring task.

Table 2 specifies the monitoring of Prairie du Chien-Jordan Aquifer monitor well W70 which is equipped with an operable dedicated submersible pump. Well purging and sample retrieval tasks will be completed with the aid of the pump in conformance with parameter monitoring established herein.

Monitoring wells and piezometers not equipped with dedicated submersible pumps will be purged using a nondedicated submersible pump, suction pump or bailer. During the purging of each well, temperature, pH, and specific conductance of the purge water will be monitored using a Hydrolab water quality monitor (or equivalent). Readings will be taken once per well volume. Stabilization of these readings will indicate that purging is complete and sampling may commence. Upon completion of well purging, samples will be collected from each well using a stainless steel or teflon bailer and a new length of nylon or polyester rope.

Samples will be collected by filling each of the appropriate sample containers in rapid succession, without prerinsing the containers with sample. The bottle will be held under the sample stream without allowing the mouth of the bottle to come in contact with the bailer and filled completely, and the cap securely tightened. All sample labels will be checked for completeness, sample custody forms completed and a description of the sampling event recorded in the field notebook.

The discharge from purging monitoring wells will be handled in accordance with the Contingency Plan (Appendix B). In general, if a visible sheen can be seen on the water surface, the discharge will be routed to the sanitary sewer. Otherwise, the storm sewer or surface water discharge will be used. Non-dedicated ground water sampling or monitoring equipment that comes in contact with the ground water will be decontaminated between uses, as described in the QAPP.

ANALYTICAL PROGRAM

Tables 1 and 2 show the ground water monitoring summary as prescribed in the RAP. Indicated on the tables are the analyses required. Expanded analyses including some priority and conventional pollutants may also be required according to RAP Section 9.3.3. Details of all analytical methodology can be found in the QAPP and it's appendices. All analyses will be performed at the Rocky Mountain Analytical Laboratory's (RMAL) Arvada, Colorado analytic facility. RMAL has agreed to provide a turnaround time of 30 working days from the receipt of samples to the submittal of analytical reports. The laboratory will notify the City of St. Louis Park if it can not meet this turnaround time.

Ground water monitoring will include two methods of PAH analyses depending upon the anticipated PAH concentration levels. Low level (nanograms per liter or part per trillion) PAH analyses will be performed utilizing selected ion monitoring (SIM) gas chromatography mass spectrometry (GC/MS). This method will be used to analyze samples from drinking water wells and from other wells for which the RAP requires drinking water criteria to be enforced (e.g., St. Peter Aquifer monitoring wells). This method is designed to analyze samples containing up to 600 nanograms per liter of an individual PAH. With dilution of the sample extract, the effective range of the method can be extended into the microgram per liter range. Specific details of this methodology can be found in Appendix B of the QAPP.

Non-criteria level (micrograms per liter or part per billion) PAH analyses, using the Scanning GC/MS Method, will be performed on samples from wells that have historically contained elevated PAH concentrations (e.g., part per million levels in well W23), and on wells that are not subject to the RAP's requirements for meeting drinking water criteria (e.g., Drift- Platteville Aquifer monitoring wells).

Two methods are required for PAH analyses because the low level part per trillion SIM method is not appropriate for samples containing more than approximately 20 micrograms per liter of total PAH. Analysis of samples containing total PAH concentrations over 20 micrograms per liter, if performed with the low level method, requires multiple dilutions and increases the risk of cross-contamination of the samples. This decreases the reliability of the data. Not only will multiple dilutions increase the variability of measurements, but critical quality control information (e.g., surrogate recoveries) is lost. Therefore, for samples containing greater than 20 micrograms per liter of total PAH the analytical method that will be used is Scanning GC/MS Method as described in the QAPP.

The Scanning GC/MS Method analysis will be performed on one-liter samples, and will have detection limits of 10 micrograms per liter. For wells that are tested with this non-criteria method, if the analytical results of historical monitoring indicate total PAH concentrations less than 20 micrograms per liter, the low level method will be used to analyze samples in 1990. This procedure will allow an evaluation of long-term PAH concentrations around the fringe PAH contamination in the Drift-Platteville Aquifer.

Depending on the circumstances and the actual PAH level, previous analytical results using the low level that exceed 20,000 nanograms per liter of total PAH will indicate a switch to the Scanning GC/MS Method for 1990 sampling rounds.

REPORTING

The analytical reporting requirements of the Consent Decree and RAP are identified in Part K of the Consent Decree, and Sections 3.4, 4.3.5, 12.1.1, and 12.1.2 of the RAP. Park K requires Reilly to submit an annual progress report on March 15, 1991. This report will contain analytical reports as specified in Section 5.0 of the QAPP for this Plan, all water level measurements and chemical analyses that have not been presented in previous reports, and interpretive maps and tables, as specified in RAP Section 3.4(B) and (C). Also the effectiveness of the source and gradient control well systems in the Drift-Platteville and St. Peter Aquifers will be discussed in the annual report.

The reporting requirement for each aquifer, and for the GAC treatment system, are described below.

GAC Treatment System

RAP Section 4.3.5 requires the City to submit an annual report that presents the results of all monitoring of the GAC treatment system. Analytical results for wellhead water, feed water, and treated water will be included in this report. The report will also describe briefly the operating performance of the GAC treatment system during the previous calendar year. The GAC treatment system annual reports are due each March 15th.

Mt. Simon-Hinckley Aquifer

The monitoring data for the Mt. Simon-Hinckley Aquifer will be included in the annual report. In addition to the results of all water level measurements and chemical analyses, the report will contain a map showing each well sampled with the concentrations of Other PAH, Carcinogenic PAH, and the sum of benzo(a) pyrene and dibenz(a,h) anthracene labelled by the location of each well in accordance with RAP Section 3.4(C). Since the Mt. Simon-Hinckley Aquifer wells are monitored on an annual basis, there will be only one sampling event to report.

Ironton-Galesville Aquifer

The monitoring data for the Ironton-Galesville Aquifer will be included in the annual report. Since well W105 is the only well that will be sampled in this aquifer and only one other well (W38) will be used for water level measurements, the monitoring data will be reported in tabular form as well as in map form as required by RAP Section 3.4.

Prairie du Chien-Jordan Aquifer

The monitoring data for the Prairie du Chien-Jordan Aquifer will be included in the annual report. The results of all water level measurements and chemical analyses will be included. For each of the quarterly measuring periods a water level contour map will be prepared with elevations labelled at each well. For each sampling event, a map showing each well sampled with the concentrations of Other PAH, Carcinogenic PAH, and the sum of benzo(a)pyrene and dibenz(a,h) anthracene labelled by the location of each well will be prepared in accordance with RAP Section 3.4(C), and a map of the area indicating the extent of PAH above drinking water criteria shall be provided.

St. Peter Aquifer

The monitoring data for the St. Peter Aquifer will be included in the annual report. The results of chemical analyses will be reported and a map showing each well sampled with the concentrations of Other PAH, Carcinogenic PAH, and the sum of benzo(a)pyrene and dibenz(a,h) anthracene labelled by the location of each well will be prepared in accordance with RAP Section 3.4.(C). Likewise, the results of water level measurements will be provided and a water level contour map will be prepared with elevations labelled at each well in accordance with RAP Section 3.4.(B). In addition, a map of the area indicating the extent of PAH above drinking water criteria shall be provided.

Drift-Platteville Aquifer

The monitoring data for the Drift-Platteville Aquifer including the results of all water level measurements and chemical analyses, will be reported. A water level contour map will be prepared with elevations labelled at each well. A map showing each well sampled with the concentrations of Other PAH, Carcinogenic PAH, and the sum of benzo(a)pyrene and dibenz(a,h)anthracene labelled by the location of each well, and a map with phenolics concentrations labelled by the location of each well will be prepared in accordance with RAP Section 3.4. The Drift-Platteville Aquifer monitoring data will be included in the annual report to support a discussion of the results with respect to the effectiveness of the source and gradient control well systems. In addition, a map of the area indicating the extent of PAH above drinking water criteria shall be provided.

QAPP/siteplan

APPENDIX A

ADDITIONAL MONITORING REQUIREMENTS

Level or Drinking Water Criterion is exceeded during the first year of operation of the system, Reilly shall immediately notify the Regional Administrator, the Director, and the Commissioner, and shall undertake such additional Monitoring as is required by Section 4.3.2.

(D) Routine Monitoring after two carbon changes shall be quarterly, unless the Regional Administrator, the Director, and the Commissioner determine that the observed service life of the carbon is too short to permit this frequency, in which case the Regional Administrator, the Director and the Commissioner shall notify Reilly of the required Monitoring frequency in accordance with Part G or H of the Consent Decree.

4.3.2. Carbon Replacement Monitoring

(A) If the analytical results from any treated water sample obtained pursuant to Section 4.3.1. exceed the Drinking Water Criterion for Other PAH or exceed the Advisory Level for either Carcinogenic PAH or the sum of benzo(a)pyrene and dibenz(a,h)anthracene, then Reilly shall collect two additional treated water samples at least 2 Days apart within one week of receiving the results of the exceedance sample. If the analytical results from either one or both of the two additional samples also exceed the Drinking Water Criterion for Other PAH or the Advisory Level for either Carcinogenic PAH or the sum of benzo(a)pyrene and dibenz(a,h)anthracene, and neither of the conditions specified in (C)(1) and (2) below are met, then the carbon shall be replaced within 21 Days of receiving the additional sample results.

(B) If the analytical results from any treated water sample obtained pursuant to Section 4.3.1. exceed the Advisory Level for Other PAH, then Monitoring of treated water shall be conducted immediately according to Section 12.1. If the results of any two samples required by Section 12.1. exceed the Drinking Water Criterion for Other PAH, and neither of the conditions specified in (C)(1) and (2) below are met, then the carbon shall be replaced within 21 Days of receiving the additional sample results.

(C) If any analytical result from the additional samples taken as required by (A) or (B) above exceeds the Drinking Water Criterion for Other PAH, or the Advisory Level for either Carcinogenic PAH or the sum of benzo(a)pyrene and dibenz(a,h)anthracene during either

(1) within one year after the carbon treatment system is placed into service or

(2) within one year after the first carbon change if carbon was changed in the first year of operation of the carbon treatment system,

then Reilly shall conduct the Monitoring program specified in Section 4.6. Reilly shall report the results of the Section 4.6. Monitoring program to the Regional Administrator, the Director and the Commissioner within 7 Days of receiving the analytical data. If the treated water from the carbon treatment system is determined pursuant to Section 4.6. to exceed the Drinking Water Criterion for Other PAH or the Advisory Levels for Carcinogenic PAH or the sum of benzo(a)pyrene and dibenz(a,h)anthracene, then Reilly shall replace the carbon within 14 Days of making this determination. If the treated water is determined pursuant to Section 4.6. to meet the Drinking Water Criterion for Other PAH and the Advisory Levels for Carcinogenic PAH and the sum of benzo(a)pyrene and dibenz(a,h)anthracene, then normal GAC system operation and Monitoring in accordance with Sections 4.3.1.(B) and

(C) After the first month of operation, Monitoring of feed water shall be performed quarterly until the carbon has been changed twice. If the Regional Administrator, the Director and the Commissioner determine pursuant to Section 4.3.1.(B) that the GAC system is not operating properly, Reilly may, upon receipt of such determination, be required to resume biweekly Monitoring of feed water.

(D) After two carbon changes in the GAC system, feed water shall be Monitored annually.

4.3.4. Extended Monitoring

Treated water from the GAC system shall be sampled and analyzed annually for the extended list of PAH in Part A.2. of Appendix A, using gas chromatography/mass spectroscopy (GC/MS), or other methods approved by the Regional Administrator and the Director. During this extended analysis, any compounds listed in Part A.2. of Appendix A, or any other compounds which are detected with significant peak heights that are not routinely Monitored, shall be identified and, if possible, quantified, using a mass spectral library which contains extensive spectra of PAH compounds, such as the National Bureau of Standards mass spectral library. Reilly shall analyze a sample of treated or feed water once a year for the acid fraction compounds determined by EPA Test Method 625 or by other methods approved by the Regional Administrator and the Director.

12.

CONTINGENT ACTIONS FOR MUNICIPAL DRINKING WATER SUPPLY WELLS

12.1. Contingent Monitoring

[redacted]

(A) three consecutive samples yield results less than all of the Advisory Levels, in which case the sampling interval shall revert to the level specified for the affected well in Sections 3., 4.3., 5.1., 6.2.1., 7.3., or 8.4. above; or

(B) a sample yields results greater than a Drinking Water Criterion, in which case the requirements of Section 12.1.2., below, apply.

12.1.2. Exceedance of Drinking Water Criteria

(A) If the analytical result of any sample taken from an active municipal drinking water well pursuant to Section 12.1.1 exceeds the Drinking Water Criterion for Carcinogenic PAH, the sum of benzo(a)pyrene and dibenz(a,h)anthracene, or Other PAH, the Regional Administrator, the Director and the Commissioner shall be immediately notified by Reilly, and another sample shall be taken by Reilly within three Days of receiving the results of the first sample and analyzed. If the analytical result of the second sample is less than all of the Drinking Water Criteria but greater than any Advisory Level, a third sample shall be taken by Reilly within seven Days of receiving the results of the second sample and analyzed. If the results of this third sample are less than all of the Drinking Water Criteria, but greater than any Advisory Level, Reilly shall comply with the monthly sampling frequency specified in Section 12.1.1. above.

(B) If the analytical result of the second or third sample taken pursuant to Section 12.1.2.(A) above is greater than the Drinking Water Criterion for Carcinogenic PAH, the sum of benzo(a)pyrene and dibenz(a,h)anthracene, or Other PAH, Reilly shall Monitor the well weekly until such time as either: (1) three consecutive samples yield results below all of the Drinking Water Criteria, in which case Monitoring of the well shall revert to the normal schedule (including Advisory Level Monitoring as specified by Section 12.1.1. above if applicable); or, (2) three consecutive samples yield results above any Drinking Water Criterion, in which case Reilly shall immediately notify the Regional Administrator, the Director and the Commissioner. The Commissioner may then require the affected well to be taken out of service, in which case Reilly shall undertake the contingent actions specified in Section 12.2. below.

12.1.3. Analytical Turn-around Time

All Monitoring conducted pursuant to Section 12.1. shall be on a 21-Day turn-around time basis in accordance with Section 2.8.

APPENDIX B

CONTINGENCY PLAN

Contingent Actions for Contaminated Water

It is possible that groundwater contaminated with coal tar materials will be encountered during the sample retrieval operations. Groundwater generated during sample retrieval operations will be classified as contaminated if the water exhibits a discernible oil sheen or oil phase. Contaminated water will be pumped to the sanitary sewer if it contains less than ten percent organic material. Estimates of flow rate, disposal volume and water quality will be established and the Metropolitan Waste Control Commission (MWCC) will be informed before the discharge to the sanitary sewer if the estimated flow exceeds 150 gallons per workday from any individual site. Contaminated liquids containing more than ten percent organic material or failing to receive MWCC approval for discharge will be disposed of in accordance with all applicable local, state and federal rules and regulations and Part T of the Consent Decree. Uncontaminated water will be disposed of in the storm sewer or by other means acceptable to the City of St. Louis Park.

The City will be responsible for keeping the Environmental Protection Agency, Minnesota Pollution Control Agency and Reilly Tar & Chemical Corporation informed of all significant actions involving the generation of contaminated groundwater. All actions, decisions and communications by the City, Environmental Protection Agency, Minnesota Pollution Control Agency, and Reilly in dealing with contaminated soils will be in accordance with and subject to the provisions of Parts I, J, and O of the Consent Decree in the Reilly settlement.

QUALITY ASSURANCE PROJECT PLAN FOR SAMPLING AND ANALYSIS - GROUNDWATER AND GAC PLANT MONITORING

Prepared by

The City of St. Louis Park
St. Louis Park, MN 55416

Approved by ______________________ Date: ______________
Gary Tort, Quality Assurance
Director, Rocky Mountain Analytical Laboratory

Approved by ______________________ Date: ______________
James N. Grube, Project Manager
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Approved by: Dale A. Goss Date: Oct. 26, 1990
Quality Assurance Officer
U.S. EPA Region V

Approved by: ______________________ Date: ______________
Remedial Project Manager
U.S. EPA Region V

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3. PROJECT DESCRIPTION

3.1 Background

Ground water in the City of St. Louis Park, Minnesota has been found to contain polynuclear aromatic hydrocarbons (PAH) and phenolics as a result of activities at a coal-tar distillation and wood preserving plant (Site) operated from 1917 to 1972. Numerous previous studies have identified PAH's in various aquifers beneath St. Louis Park and adjacent communities. Accordingly, the site of the plant operations was placed on the National Priorities List and the federal and state governments sought remediation of environmental contamination via United States District Court Case No. Civil 4-80-469.

A summary of the aquifers which underly the former wood preserving plant site, their approximate location below the surface level, the general use of the aquifers, and the relative maximum historical PAH and phenolics concentrations measured in each unit (as indicated by historical records and the federal government's Record of Decision in Case No. Civil 4-80-469) are as follows:

Aquifer	Approximate Depth (ft.)	Use	Approximate Upper Concentration of Total PAH's	Approximate Upper Concentration of Phenolics
Drift-Platteville	0 - 90	Private/Industrial/ Monitor wells	1000 ug/l offsite	10,000 ug/l offsite
St. Peter	90 - 200	Municipal/Private drinking water wells	10 ng/l offsite	16 ug/l offsite
Prairie du Chien-Jordan	250 - 500	Municipal drinking water wells	10 ug/l offsite	10 ug/l offsite
Ironton-Galesville	700 - 750	Industrial	1.4 ug/l onsite	5 ug/l offsite
Mt. Simon-Hinckley	800 - 1100	Municipal drinking water wells	16 ng/l offsite	Not detected

More extensive information relative to the identified level of PAH's in the various aquifers is provided in the following reports:

- Annual Monitoring Reports for 1988 and 1989
- St. Peter Aquifer Remedial Investigation Report (March 30, 1989)
- Drift-Platteville Aquifer (Northern Area) Remedial Investigation Report (March 30, 1989)

The United States Environmental Protection Agency (EPA), the Minnesota Pollution Control Authority (MPCA), the Minnesota Department of Health (MDH), the City of St. Louis park (City), and Reilly Industries, Inc. (formerly Reilly Tar & Chemical Corporation - Reilly) have agreed to acceptable water quality criteria for PAH. These criteria, as incorporated into the Consent Decree - Remedial Action Plan (RAP), in the case referenced above include the following concentration levels:

	Advisory Level	Drinking Water Criteria
o Sum of benzo(a) pyrene and dibenz(a,h) anthracene	3.0 ng/l*	5.6 ng/l
o Carcinogenic PAH	15 ng/l	28 ng/l
o Other PAH	175 ng/l	280 ng/l

*or the lowest concentration that can be quantified, whichever is greater

Table 3-1 lists the nominal reporting limits for the target compounds listed in the Consent Decree-RAP.

In conjunction with the implementation of remedial measures to limit the spread of contaminants, a granular activated carbon (GAC) treatment system has been installed to treat water from City wells (identified - SLP) 10 and 15. Further provisions of the RAP call for long term monitoring of the influent and effluent of the GAC treatment system and the major aquifers underlying the region. The general objective of the monitoring program is to identify the distribution of PAH and/or phenolics in the ground water and compare the analytical data with water quality criteria established in the Consent Decree-RAP. The specific objectives of the sampling and analysis program, and therefore, the intended end use of the data varies slightly for the different aquifers (Mt. Simon-Hinckley, Ironton-Galesville, Prairie du Chien-Jordan, St. Peter, and Drift-Platteville) being monitored in accordance with the Consent Decree-RAP.

3.2 Objectives and Intended Data Usage

Analytical levels for this project incorporate aspects of levels IV, and V, as defined by "Data Quality Objectives for Remedial Response Activities" (U.S. EPA, 1987). Data use categories include monitoring during implementation, site characterization, and risk assessment. It is the level of concern for low part-per-trillion concentrations of PAH that specifies a level V analytical level for this project. Level V includes non-conventional parameters, method-specific detection limits, and the modification of existing analytical methods. Rigorous QA/QC to produce data of known quality are part of this program.

The objective of the GAC treatment system monitoring is to assess and evaluate the performance of the treatment system. Analytical results for influent and effluent samples will be compared to the drinking water criteria for PAH as established in the Consent Decree-RAP. Based on these comparisons, decisions will be made on: 1) system operations (e.g., when the carbon should be replaced), and 2) cessation of the treatment system, if desired, when sufficiently low concentrations of PAH in influent samples are demonstrated.

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TABLE 3-1
TABLE OF REPORTING LIMITS FOR TESTED PARAMETERS

CAS Number	Compound	Reporting Limit ng/L (PPT)	Reporting Limit ug/L (PPB)
271-89-6	2,3-Benzofuran	5.1	10
496-11-7	2,3-Dihydroindene	1.4	10
95-13-6	1H-Indene	0.9	10
91-20-3	Naphthalene	6.5	10
4565-32-6	Benzo(b)thiophene	0.9	10
91-22-5	Quinoline	1.4	10
120-72-9	1H-Indole	2.5	10
91-57-6	2-Methylnaphthalene	0.9	10
90-12-0	1-Methylnaphthalene	1.6	10
92-52-4	Biphenyl	4.3	10
208-96-8	Acenaphthylene	1.4	10
83-32-9	Acenaphthene	1.3	10
132-64-9	Dibenzofuran	1.0	10
86-73-7	Fluorene	1.0	10
132-65-0	Dibenzothiophene	1.1	10
85-01-8	Phenanthrene	1.3	10
120-12-7	Anthracene	1.1	10
260-94-6	Acridine	2.9	10
86-74-8	Carbazole	1.9	10
206-44-0	Fluoranthene	1.4	10
129-00-0	Pyrene	1.4	10
56-55-3	Benzo(a)anthracene	2.5	10
218-01-9	Chrysene	2.8	10
205-99-2	Benzo(b)fluoranthene	2.5	10
207-08-9	Benzo(k)fluoranthene	2.3	10
192-97-2	Benzo(e)pyrene	1.9	10
50-32-8	Benzo(a)pyrene	2.3	10
198-55-0	Perylene	2.5	10
193-39-5	Indeno(1,2,3-cd)pyrene	2.1	10
53-70-3	Dibenz(a,h)anthracene**	1.6	10
191-24-2	Benzo(g,h,i)perylene	2.8	10
205-82-3	Benzo(j)fluoranthene***	--	--
195-19-7	Benzo(c)phenanthrene*	--	--
215-58-7	Dibenz(a,c)anthracene**	1.6	--
192-65-4	Dibenzo(a,e)pyrene*	--	--
189-64-0	Dibenzo(a,h)pyrene*	--	--
189-55-9	Dibenzo(a,i)pyrene*	--	--
57-97-6	7,12-Dimethylbenz(a)anthracene	2.8	--

TABLE 3-1 (continued)

CAS Number	Compound	Reporting Limit ng/L (PPT)	Reporting Limit ug/L (PPB)
56-49-5	3-Methylcholanthrene	3.5	--
108-95-2	Phenol	--	10
95-48-7	2-Methylphenol	--	10
106-44-5	4-Methylphenol	--	10
95-57-8	2-Chlorophenol	--	10
88-75-5	2-Nitrophenol	--	10
105-67-9	2,4-Dimethylphenol	--	10
120-83-2	2,4-Dichlorophenol	--	10
59-50-7	4-Chloro-3-methylphenol	--	10
88-06-2	2,4,6-Trichlorophenol	--	10
95-95-4	2,4,5-Trichlorophenol	--	50
51-28-5	2,4-Dinitrophenol	--	50
100-02-7	4-Nitrophenol	--	50
534-52-1	4,6-Dinitro-2-methylphenol	--	50
87-86-5	Pentachlorophenol	--	50
	Total Phenolics	--	5

* No analytical standard available

** Dibenz(a,h)anthracene and Dibenz(a,c)anthracene coelute

*** Laboratory studies have shown that Benzo(j)fluoranthene will coelute with either benzo(b)fluoranthene or benzo(k)fluoranthene depending on the relative concentration of these two compounds in solution. Benzo(j)fluoranthene can not be consistently separated by this method. Therefore if present, it will be detected and reported as benzo(b) and/or benzo(k)fluoranthene.

The objective of monitoring the four existing Mt. Simon-Hinckley Aquifer municipal drinking water wells and any new Mt. Simon-Hinckley Aquifer municipal drinking water wells installed within one mile of well W23, and analyzing for PAH, is to assure the continued protection of these wells from PAH resulting from activities of Reilly at the Site. The analytical data will be used to make comparisons between the levels of PAH found in the Mt. Simon-Hinckley Aquifer, and the drinking water criteria established in the Consent Decree-RAP.

The objective of monitoring the Ironton-Galesville Aquifer source control well (W105) is to assess the levels of PAH in the discharge from W105 when it is pumping a monthly average of 25 gallons per minute. The data will be used to compare the concentration of total PAH in the samples to a cessation criterion of 10 micrograms per liter of total PAH established in the Consent Decree-RAP. In the event monitoring results indicate the water quality has improved to within cessation criterion, the City will petition the EPA and MPCA for authorization to discontinue the pumping of W105. Also, if any new Ironton-Galesville Aquifer drinking water wells are installed within one mile of well W23, then those wells will be sampled and analyzed for PAH to meet the objective of assuring protection of the wells from PAH resulting from the activities of Reilly at the Site. The analytical data would be used to compare the levels of PAH found in potential Ironton-Galesville Aquifer drinking water wells to the drinking water criteria established in the Consent Decree-RAP.

The objectives of monitoring the many Prairie du Chien-Jordan Aquifer wells, including municipal drinking water wells, private or industrial wells, and monitoring wells are to: 1) monitor the distribution of PAH in the aquifer, thus evaluating the source and gradient control system, and 2) assure the continued protection of drinking water wells from PAH resulting from the activities of Reilly at the Site. The analytical data will be used to compare the levels of PAH in the Prairie du Chien-Jordan Aquifer to historical PAH data and to various criteria established in the Consent Decree-RAP (e.g., drinking water criteria for drinking water wells, and a cessation criterion of 10 micrograms per liter of total PAH for source control well W23).

In addition to water quality data generation, water level data will be used for the purpose of determining ground water flow patterns in the Prairie du Chien-Jordan Aquifer.

The objectives of monitoring St. Peter Aquifer wells are to: 1) monitor the distribution of PAH in the aquifer, thus evaluating a gradient control system installed at W410 in 1990, and 2) assure the continued protection of drinking water wells from PAH resulting from the activities of Reilly at the Site.

Upon its receipt analytical data will be used to compare the levels of PAH in the St. Peter Aquifer to historical PAH data, to drinking water cessation criteria for well W410, and to drinking water criteria established in the Consent Decree-RAP. Water level data will be used to evaluate ground water patterns in the St. Peter Aquifer.

The objective of monitoring the Drift-Platteville Aquifer wells is to monitor the distribution of PAH and phenolics in the aquifer, thus evaluating the source and gradient control systems. The analytical data will be used to compare levels of PAH and phenolics in the Drift-Platteville Aquifer with historical water quality data for the aquifer and with various criteria established in the Consent Decree-RAP for PAH and phenolics. Water level data will be used to evaluate ground water flow patterns in the Drift-Platteville Aquifer.

In addition to the objectives for laboratory analytical data described above, field measurement data will be collected to aid in the ground water sampling procedure. In accordance with Minnesota Pollution Control Agency Guidelines (April, 1985) field measurements of temperature, pH, and specific conductance will be made for the purpose of determining that a sufficient volume of water has been purged from the well prior to sampling. The objective of those field measurements is to determine when three successive well volumes exhibiting equivalent temperature pH, and specific conductance have been purged from each monitoring well, so that representative samples may be collected.

The Site Management Plan outlines the scope of work to be performed in order to monitor the ground water in the St. Louis Park, Minnesota area in accordance with the Consent Decree-RAP related to the Reilly Tar & Chemical Corporation N.P.L. Site. Included in this plan are: 1) the identity of wells to be monitored, 2) the schedule for ground water monitoring, and 3) a description of the procedures that will be used for sample collection, water level measurement, sample handling, sample analysis, and reporting.

The time period covered by this Plan is from January 1, 1990, or the date of its acceptance and approval by the Agencies whichever is later, to December 31, 1990. The next subsequent Sampling Plan (RAP Section 3.3) will be submitted by October 31, 1990, covering the 1991 calendar year.

4. PROJECT ORGANIZATION AND RESPONSIBILITIES

This project is being conducted in accordance with the Consent Decree-RAP for the Reilly Tar & Chemical Corporation N.P.L Site in St. Louis Park, Minnesota. The parties to the Consent Decree include Reilly, the City, EPA, MPCA, and MDH. The project organization shown in Figure 4-1 indicates the involvement of the parties to the Consent Decree, as appropriate. The City is responsible for the completion of the monitoring tasks described in this Plan. The City's Project Manager is responsible for overall project management. The City shall be assisted by two consultants in the retrieval and laboratory analysis of water samples.

ENSR Consulting and Engineering (ENSR) will be responsible for the coordination of all field sample retrieval and Enseco/Rocky Mountain Analytical Laboratory (RMAL), with analytical facilities in Arvada, Colorado, will be responsible for the coordination and completion of all laboratory analyses. Responsibilities of the key positions in the organization of RMAL are described below:

- Laboratory Project Manager: The Laboratory Project Manager is ultimately responsible for all laboratories and is the primary point of contact for issues surrounding this Quality Assurance Project Plan (QAPP), resolving technical problems, modifications to Standard Operating Procedures (SOP's) etc.

- Laboratory Project Coordinator: The Laboratory Project Coordinator is responsible for the cordination of routine day to day project activities including project initiative, status tracking, data review and requests, inquiries and general communication related to the project.

- Operations Manager: The Operations Manager is responsible for oversight of preparation and analysis of PAH samples to ensure that project objectives, requirements and Quality Assurance/Quality Control (QA/QC) criteria are met.

- Laboratory Supervisor: The Laboratory Supervisor shall be responsible for daily supervision of technicians and analysts for PAH and total phenolics analyses.

- Preparation Supervisor: The Preparation Supervisor is responsible for oversight of sample extraction and preparation for analysis.

- Analyst: The Analyst is responsible for the analysis of water samples for the requested parameters utilizing the methods prescribed by the QAPP.

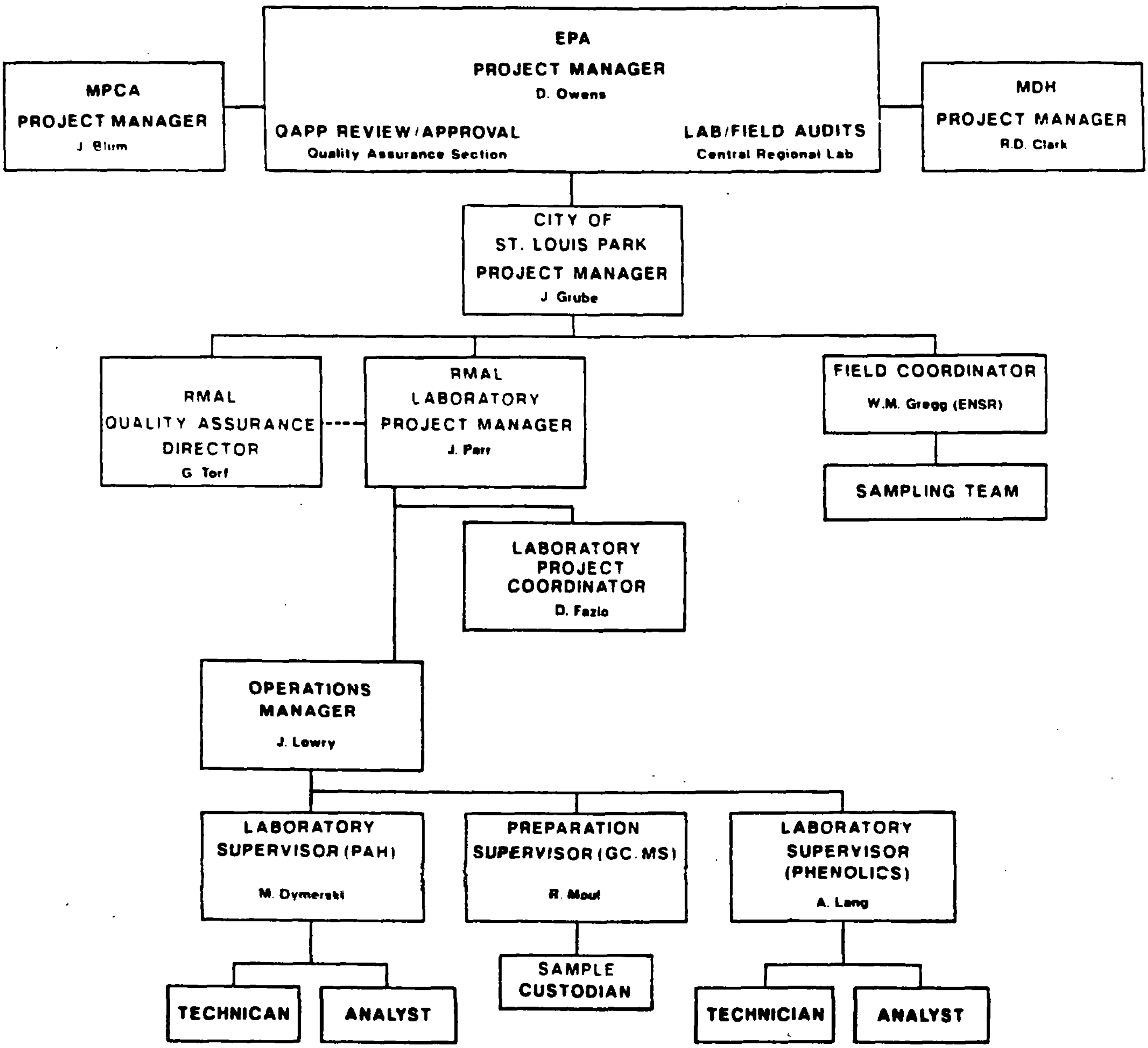

Figure 4-1 Project Organizational Chart

- Technician: The Technician is responsible for sample extraction. This requires practical experience and knowledge in the techniques of liquid - liquid solvent extraction, Kuderna - Danish evaporation, and the quantitative preparation of sample extracts for analysis.

- Quality Assurance Director: The Quality Assurance Director is responsible for overall quality control oversight, including internal audits. The Quality Assurance Director supervises an independent QA/QC department and reports directly to the Division Director and Corporate Vice President for Quality Assurance.

- Data Assessment: The evaluation of data, as it is compiled and organized in accordance with the requirements of the QAPP, is the responsibility of the Operations Manager. Additional review, evaluation, and assessment of the data is performed by the Laboratory Manager, thereby providing additional assurance that the requirements of the QAPP are met.

  The City's Project Manager shall be responsible to assess the data relative to the objectives and intended data usage identified in Section 3.2. of this QAPP.

The Sampling Team shall consist of employees of the City of St. Louis Park and ENSR. The team shall be responsible for sample collection, conducting field measurements (i.e. water level), and maintaining proper decontamination procedures stated in the QAPP.

The EPA and MPCA are responsible for review and approval of the Sampling Plan, including the QAPP. In addition, laboratory and field audits may be completed by appropriate EPA representatives. The MPCA is responsible for review of field procedures practiced by the Sampling Team. Responsibilities of the key positions in the EPA and MPCA are described below:

- EPA Project Manager: The EPA Project Manager, EPA Region 5, is responsible for the review and approval of the QAPP on behalf of the EPA.

- EPA Quality Assurance Officer: The EPA Quality Assurance Officer, EPA Region 5, is responsible for the review and approval of the QAPP on behalf of the EPA.

- EPA Central Regional Laboratory: The EPA Central Regional Laboratory, EPA Region 5, shall be responsible for audits of both field activities and laboratory analyses.

- MPCA Project Manager: The MPCA Project Manager shall be responsible for review and approval of the Sampling Plan, and review of field procedures practiced by the Sampling Team.

5. QUALITY ASSURANCE OBJECTIVES

The principal objectives of the QAPP pertain to the collection of data that are sufficient to monitor the effectiveness of the GAC treatment system and to detect changes in groundwater quality. Therefore, the quality of the data gathered in this project can be defined in terms of the following elements:

- Completeness - a sufficient number of successful (valid) measurements to characterize the concentrations of PAH in the influent and effluent of the treatment system and in the aquifers of interest over a period of time. For this project, the completeness objective is that 95% of the laboratory analyses and 95% of the field measurements will produce valid data. Field data will be supplemented by resampling if necessary to ensure completeness.

- Representativeness - the extent to which reported analytical results truly depict the PAH and phenolics concentrations in the sampled environment. Representativeness is optimized through proper selection of sampling sites, times and procedures, through proper sample preservation, and through prompt extraction and analysis.

- Accuracy and Precision - Accurate and precise data will be achieved through the use of sampling and analytical procedures that minimize biases, through the use of standard procedures, through the meticulous calibration of analytical equipment and by implementing corrective action whenever measured accuracy and precision exceed pre-established limits. Accuracy and precision will be measured by the analysis of method spikes and duplicate samples.

  It is essential that representative ground water samples be retrieved for laboratory analyses. Accuracy and precision in the measurement of parameters used to monitor ground water as it is purged from monitor wells and piezometers will be achieved through the use of standard monitoring procedures carried out continuously during the sample retrieval task. Field measurement equipment will be calibrated in accordance with the manufacturer's recommendations, as outlined in Table 6-6, and appropriate corrective action will be initiated whenever measured accuracy and precision do not meet pre-established limits. Since precision and accuracy of field measurement devices are not primary objectives for the data, the quality control requirements are sufficient for the intended use of the field measurement data.

- Sensitivity - Determination of instrument sensitivity is accomplished by calibration using multiple concentrations of the analytes of interest. Once instrument sensitivity is demonstrated, analysis of replicate spiked samples of deionized reagent water at a concentration of 1-5 times the instrument sensitivity, is used to determine method sensitivity (i.e. method detection limit).

- o Comparability - the extent to which comparisons among separate measurements will yield valid conclusions. Comparability among measurements in the monitoring program will be achieved through the use of rigorous standard sampling and analytical procedures.

- o Traceability - the extent to which results can be substantiated by hard-copy documentation. Traceability documentation exists in two forms: that which links final numerical results to authoritative measurement standards, and that which explicitly describes the history of each sample from collection to analysis.

The fundamental mechanisms that will be employed to achieve these quality goals can be categorized as prevention, assessment and correction, as follows:

1) Prevention of defects in the quality through planning and design, documented instructions and procedures, and careful selection and training of skilled, qualified personnel;

2) Quality assessment through a program of regular audits and inspections to supplement continual informal review (refer to Section 12 of this QAPP);

3) Permanent correction of conditions adverse to quality through a closed-loop corrective action system.

The St. Louis Park sampling program QAPP has been prepared in direct response to these goals. The QAPP describes the quality assurance program to be implemented and the quality control procedures to be followed by RMAL during the course of laboratory analyses in support of the various site investigation studies for the St. Louis Park Site. The Quality Assurance objectives will include field blanks, method blanks, field duplicates, surrogate spikes, matrix spikes and matrix spike duplicates. Precision, accuracy and completeness criteria are established for each parameter of interest. The specific criteria for each analysis and parameter are set forth in detail in the following sections:

Objective	Frequency	Sections Discussing Criteria
Field Duplicates	10%	6.8, 11.1.4
Field Blanks	10%*	6.5.2
Method Blanks	5%*	11.1.1, 15.1.3
Surrogate Spikes	100% of GC/MS analyses	11.1.2, 15.1.1
Matrix Spikes/Duplicates	5%*	11.1.3, 15.1.2

* One per group of 20 or fewer investigative samples.

6. SAMPLING PROCEDURES

Samples will be collected by ENSR and City personnel in accordance with MPCA guidelines (MPCA, 1985; Appendix A). The overall sampling program is summarized in Tables 6-1, 6-2, and 6-3, and Figures 6-1 through 6-5. This section discusses general QAPP provisions relevant to sample collection, containerization, packaging and shipping activities (SOPs 7130 and 7510; Appendix A).

6.1 Training

All ENSR and City personnel working on the project will be properly trained, qualified individuals. Prior to commencement of work, personnel will be given instruction specific to this project, covering the following areas:

- Organization and lines of communication and authority
- Overview of the Site Management Plan and QAPP,
- Documentation requirements,
- Decontamination requirements,
- Health and Safety considerations.

Training of field personnel will be provided by the Field Coordinator or a qualified designee.

The analysts performing chemical analyses of samples will be trained in and will have exhibited proficiency in the analytical methods to be employed.

6.2 Document Control

Document Control for the Sampling Plan serves a two-fold purpose. It is a formal system of activities that ensures that:

1) All participants in the project are promptly informed of revisions of the QAPP; and

2) All documents generated during the course of the program are accounted for during, and at the end of the project.

This QAPP and all Standard Operating Procedure documents have the following information on each page:

- Document Number
- Page Number
- Total number of pages in document
- Revision number
- Revision date

TABLE 6-1
SUMMARY OF SAMPLING AND ANALYTICAL PROGRAM

Sample Matrix	Field Parameter	Number of Samples	Laboratory Parameters	Number of Samples	Field Blanks	Field Duplicates	Matrix Spike[b]	Matrix Spike Duplicate[b]	Matrix Total
GAC Treated Water	X	X	PAH (ppt)	4	4	4	4	4	20
			Acid Fraction compounds[a]	1	X	1	1	1	4
GAC Feed Water	X	X	PAH (ppt)	1	X	1	1	1	4
Ground water	pH	107	PAH (ppt)	74	18	22	17	17	148
	temperature		PAH (ppb)	22	4	4	4	4	38
	Specific Conductance		Total Phenols	36	9	9	8	8	70

(a) Analysis of sample for acid fraction compounds listed in EPA Method 625 shall be in accordance with CLP SOW-2/88.

(b) Matrix spike sample/matrix spike duplicate sample shall consist of the same matrix being analyzed. Triple the normal volume when related matrix spike/matrix spike duplicate samples are to be retrieved.

TABLE 6-2
SAMPLING PLAN GAC PLANT
MONITORING SCHEDULE[a]

RAP Section	Sampling Points	Start of Monitoring	Sampling Frequency	Analyses[b]
4.3.1(C)	Treated water(TRTD)	Date of plan approval	Quarterly	PAH(ppt)[c]
4.3.3(C)	Feed water(FEED)	Date of plan approval	Annually	PAH(ppt)
4.3.4	Treated water	Date of plan approval	Annually	Extended PAH(ppt)
4.3.4	Treated or Feed water	Date of plan approval	Annually	Acid fraction compounds in EPA Test Method 625.

(a) This schedule does not include certain contingencies (eg. exceedance monitoring) and, therefore, represents the minimum program that is likely to occur between the date this Plan is approved and December 31, 1990. Sections 4 and 12 of the RAP outline the additional sampling that will be conducted if PAH criteria are exceeded. The first samples will be collected during the period indicated by the monitoring frequency following the date of the start of monitoring. The location of the GAC plant is shown in Figure 6-1.

(b) List of parameters and methods for analysis of PAH, extended PAH, and acid fraction compounds in EPA Test Method 625 are provided in the QAPP. Field blanks will be collected and analyzed at a frequency of one for every 10 samples or fewer. Treated water will be duplicated at a rate of 100%. Feed water duplicate samples will be collected and analyzed at a frequency of one per 10 samples.

(c) ppt = parts per trillion. This signifies analysis using selected ion monitoring gas chromatography mass spectrometry.

TABLE 6-3
SAMPLING PLAN GROUND WATER
MONITORING SCHEDULE [a]

Source of Water	RAP Section	Sampling Points [b]	Start of Monitoring	Sampling Frequency	Analyses [c]	Duplicate Samples
Mt. Simon-Hinckley Aquifer	5.1	SLP11, SLP12, SLP13, SLP17	Date of plan approval	Annually	PAH(ppt) [d]	SLP12 SLP17
	5.3.2	New municipal wells within one mile of well W23	At the time of installation	Annually	PAH(ppt)	
Ironton-Galesville Aquifer	6.1.4	W105 W38 [e]	Date of plan approval	Quarterly	PAH(ppt)	W105
	6.2.1	New municipal wells within one mile of well W23	At the time of installation	Annually	PAH(ppt)	
Prairie du Chien-Jordan Aquifer	7.3(A) [f]	SLP4	Start of pumping	Quarterly	PAH(ppt) phenolics	SLP4
	7.3(B) [f]	W23	Date of plan approval	Semi-annually	PAH(ppb) [g]	
	7.3(C) [f]	SLP6, SLP7 or SLP9, W48	Date of plan approval	Quarterly	PAH(ppt)	SLP6
	7.3(D) [f]	W405 or W406 [h] E2, E13, H3, SLP10 or SLP15, SLP14, SLP16, W402 W403, W119	Date of plan approval	Semi-annually	PAH(ppt)	SLP16
	7.3(E) [f]	SLP5, H6, E3, E15, MTK6, W29, W40, W70, W401	Date of plan approval	Annually	PAH(ppt)	W70

TABLE 6-3 (Continued)

Source of Water	RAP Section	Sampling Points[b]	Start of Monitoring	Sampling Frequency	Analyses[c]	Duplicate Samples
	7.3(F)	W32, SLP8, SLP10, E4, E7	Date of plan approval	Quarterly	No Chemical analyses[i]	
St. Peter Aquifer	8.1.3	SLP3, W11, W33, W129, W133, W408, W409	Date of plan approval	Semi-annually	PAH(ppt)	
Drift-Platteville Aquifer	9.1.3 and 9.2.3	W420, W421, W422	Date of plan approval	Quarterly	PAH(ppb) and total phenols	W422
	9.6	Drift: W10, W15, W116, W117, W128, W423, W427, P109, P112, P306, Platteville: W20, W22, W101, W121, W124, W130, W132, W424, W428, W430	Date of plan approval	Annually[j]	PAH(ppb)/(ppt) and total phenols	W121

(a) This schedule does not include certain contingencies (e.g. exceedance monitoring) and, therefore, represents the minimum program that is likely to occur between the date this Plan is approved and December 31, 1990. Section 12 of the RAP outlines the additional sampling that will be conducted if the drinking water criteria are exceeded in samples from water supply wells. The first samples will be collected during the period indicated by the monitoring frequency following the date of the start of monitoring. Field blanks will be collected at a frequency of one for every 10 samples or fewer, and one duplicate sample will be collected for every 10 samples.

TABLE 6-3 (Continued)

(b) Sampling points are located on the maps shown in Figures 1 through 5. Letter prefixes to well codes are defined as follows:

W - 4-inch monitoring well
P - monitoring piezometer
SLP - St. Louis Park supply well
E - Edina supply well
H - Hopkins supply well
MTK - Minnetonka supply well

(c) Lists of parameters and descriptions of the methods for analysis of PAH, phenolics, and expanded analyses are provided in the QAPP. Water levels will be measured each time samples are collected for analysis, except for those wells which prove to be inaccessible for such measurements.

(d) ppt = parts per trillion. This signifies analysis using selected ion monitoring gas chromatography mass spectrometry.

(e) Water levels in W38 will be measured each time W105 is sampled.

(f) Water levels only will be measured at these wells, except for those wells which prove to be inaccessible for such measurements.

(g) ppb = parts per billion. This signifies analysis by the Non-Criteria Method. If analytical results for individual wells are below 20 micrograms per liter (20 ppb) using this method, then the Low-Level Method will be used on subsequent monitoring rounds.

(h) W405 = American Hardware Mutual, W406 = Minikahda Golf Course.

(i) Water levels only (no monitoring) will be measured at these wells, except for those wells which prove to be inaccessible for such measurements. (NOTE: W112 has been properly abandoned and no longer be included in this or subsequent Plans.)

(j) If any of the wells listed here become damaged, destroyed, or otherwise unsuitable for sampling, alternate wells will be selected by the Project Leaders for monitoring.

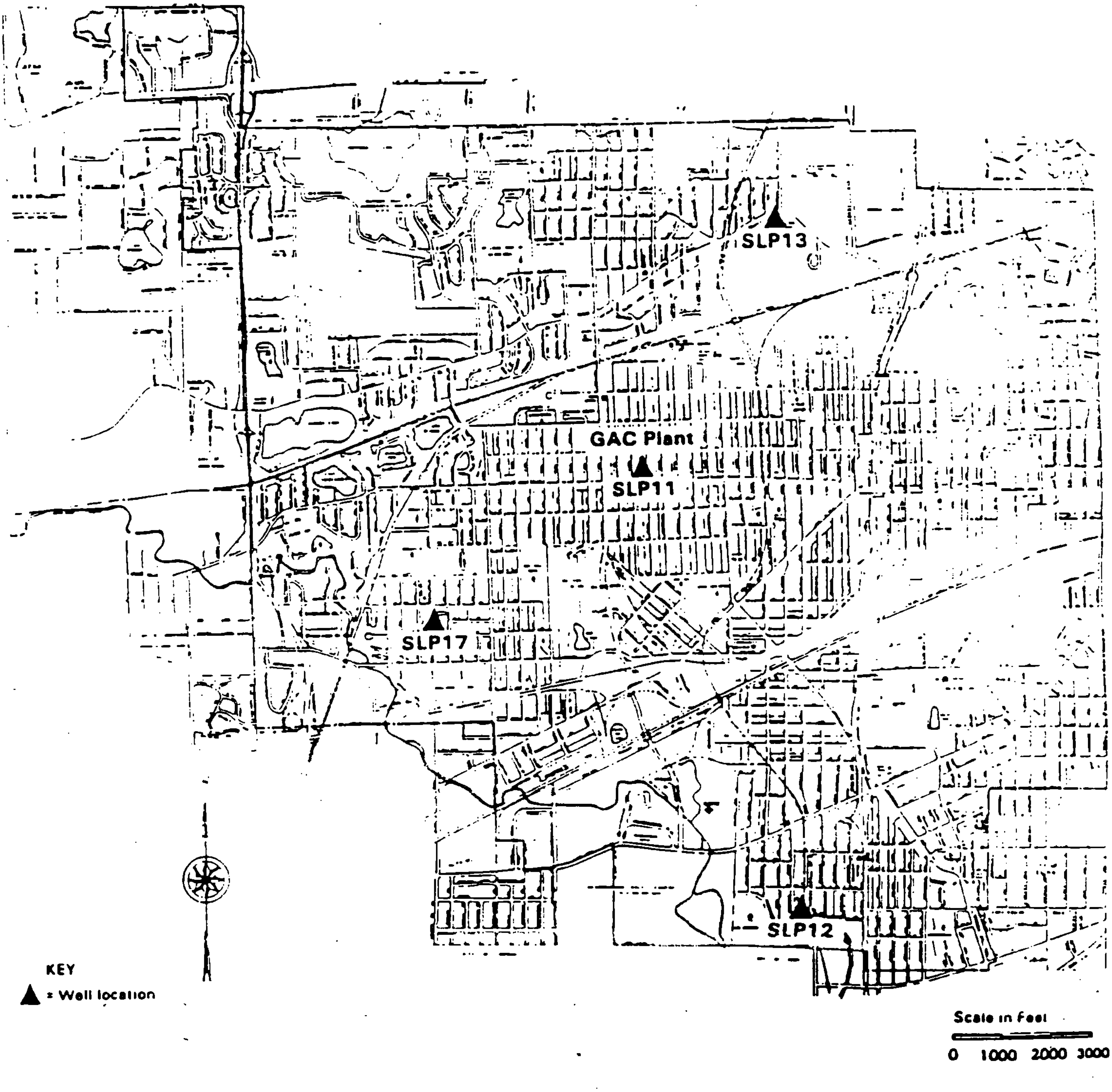

Figure 6-1 Location of Mt. Simon-Hinkley Monitoring Wells and St. Louis Park GAC Water-Treatment Plant

[redacted]

NON-RESPONSIVE

Figure 6-2 Location of Prairie du Chien-Jordan Aquifer Wells

[redacted]

NON-RESPONSIVE

0 500 1000

Figure 6-3 Location of Source and Gradient Control Wells

[redacted]

NON-RESPONSIVE

0 500 1000 2000
FEET

N

EXPLANATION

● DRIFT WELLS

■ PLATTEVILLE WELLS

Figure 6-4 Location of Drift-Platteville Monitoring Wells

Reference: MGS, Miscellaneous Map Series,
M-57, Plate 1 of 2, Bedrock Geology,
[redacted]

NON-RESPONSIVE

0 ½ MILE

EXPLANATION

▲W33 LOCATION AND PROJECT WELL NUMBER

▲ OBSERVATION WELL COMPLETED IN ST. PETER AQUIFER

■ OBSERVATION WELL COMPLETED IN BASAL ST. PETER CONFINING BED

⊙ ST. PETER AQUIFER CONTROL WALL W410

BEDROCK VALLEY/CONTACT WHERE UNCONSOLIDATED DRIFT DEPOSITS OVERLIE ST. PETER SANDSTONE

Figure 6-5 St. Peter Aquifer Well Locations and Bedrock Valley

When any of these documents are revised, the affected pages are reissued to all personnel listed as document holders with updated revision numbers and dates. Issuance of revisions is accompanied by explicit instructions as to which documents or portions of documents have become obsolete.

Control of, and accounting for documents generated during the course of the project is achieved by assigning the responsibility for document issuance and archiving. Table 6-4 lists the key documentation media for the project and corresponding responsible parties for issuance, execution and archiving.

6.3 Sample Control Procedures and Chain of Custody

In addition to proper sample collection, preservation, storage and handling, appropriate sample identification procedures and chain of custody are necessary to help insure the validity of the data.

6.3.1 Sample Identification

Sample labels shall be completed for each sample, using waterproof ink, unless prohibited by weather conditions. For example, a logbook notation would explain that a pencil was used to fill out the sample tag because a ballpoint pen would not function in freezing weather. The information recorded on the sample label includes:

Sample Number - Unique coded sample identification number as described below.

Time - A four-digit number indicating the military time of collection.

Sampler - Signature of person collecting the sample.

Remarks - Any pertinent observations or further sample description. The sample number includes three parts (source code, sampling point code, and date code) in the following sequence:

XXX-YYYYY-ZZZZZZ

TABLE 6-4
DOCUMENT CONTROL

Item	Issued By	Issued To	Archived By
Field Notebooks	Field Coordinator	Sampling Team	Field Coordinator
Field Equipment Calibration Forms	Field Coordinator	Sampling Team	Field Coordinator
Sample Logs	Field Coordinator	Sampling Team	Field Coordinator
Chain-of-Custody Forms	Lab Sample Custodian	Field Coordinator	Lab Sample Custodian
Sample Labels	Field Coordinator	Sampling Team	Lab Sample Custodian

XXX	= Source Code	
	GAC Treatment System	= GAC
	Mt. Simon-Hinckley Aquifer	= MSH
	Ironton-Galesville Aquifer	= IGV
	Prairie du Chien-Jordan Aquifer	= PCJ
	St. Peter Aquifer	= STP
	Drift-Platteville Aquifer	= DPV

YYYYY = Sampling Point Code
Well identification as abbreviated in Tables 6-2 and 6-3

ZZZZ = Date Code
Month, day, year

Those samples which will be taken in accordance with this QAPP for quality control purposes will be identified by appending to the sampling point codes the following:

Field blank = FB
Field duplicate = D
Matrix spike = MS
Matrix spike duplicate = MSD

As an example, a field blank sample taken for the Mt. Simon-Hinckley Aquifer,sampling point SLP11 on 1 January 1990 would be identified as follows:

MSH-SLP11FB-010190

During the sampling event, one sample will be taken per sampling point unless it is duplicated. Duplicate samples will be collected as specified in Tables 6-2 and 6-3. Those samples collected for matrix spike analysis will be selected at the time of sampling and labelled in the field.

Ater collection, identification, and preservation, the sample will be maintained under chain-of-custody procedures discussed below.

6.3.2 Chain-of-Custody Procedures

To maintain and document sample possession, chain-of-custody procedures will be followed. A sample is under custody if:

- It is in someone's possession, or
- It is in someone's view, after being in their possession, or
- It was in someone's possession and they locked it up to prevent tampering, or
- It is in a designated secure area.

Samples are accompanied by a Chain-of-Custody Record (Figure 6-6). When transferring the possession of samples, the individuals relinquishing and receiving will sign, date, and note the time on the record. This record documents sample custody transfer from the sampler, often through another person, to the analyst at the laboratory.

Minimum information recorded on the chain-of-custody record in addition to the signatures and dates of all custodians will include:

- o Sampling site indentification
- o Sampling date and time
- o Identification of sample collector
- o Sample identification
- o Sample description (type and quantity)
- o Analyses to be performed.

Samples will be packaged properly for shipment and dispatched to the appropriate laboratory for analysis, with a separate custody record accompanying each shipment. Shipping containers will be sealed for shipment to the laboratory. The method of shipment, courier name(s) and other pertinent information are entered in the "Remarks" box. Then tear off the last copy of the form and place the original and remaining copies in the container. After the container is closed, place the custody seals on the container.

Whenever samples are split with another laboratory, it is noted in the "Remarks" section. The note indicates with whom the samples are being split and is signed by both the sampler and recipient. If either party refuses a split sample, this will be noted and signed by both parties. The person relinquishing the samples to the facility or agency should request the signature of a representative of the appropriate party, acknowledging receipt of the samples. If a representative is unavailable or refuses to sign, this is noted in the "Remarks" space. When appropriate, as in the case where the representative is unavailable, the custody record should contain a statement that the samples were delivered to the designated location at the designated time.

6.3.3 Field Forms

In addition to sample labels and chain-of-custody forms, a bound field notebook will be maintained by the sample team leader to provide a daily record of significant events. Information to be documented in the notebook will be ground water sample collection records, calibration records, list of samples

Enseco - Rocky Mountain Analytical
4955 Yarrow Street
Arvada, Colorado 80002
303/421-6611 Facsimile 303/431-7171

CHAIN OF CUSTODY

No. 5001

Attn: ____________

Enseco Client ____________

Project ____________

Sampling Co. ____________

Sampling Site ____________

Team Leader ____________

SAMPLE SAFE™ CONDITIONS

1. Packed by: ____________ Seal # ____________
2. Seal Intact Upon Receipt by Sampling Co Yes No
3. Condition of Contents ____________
4. Sealed for Shipping by ____________
5. Initial Contents Temp ________ °C Seal # ____________
6. Sampling Status: Done Continuing Until ____________
7. Seal Intact Upon Receipt by Laboratory Yes No
8. Contents Temperature Upon Receipt by Lab ________ °C
9. Condition of Contents ____________

Date	Time	Sample ID/Description	Sample Type	No. Containers	Analysis Parameters	Remarks

CUSTODY TRANSFERS PRIOR TO SHIPPING

	Relinquished by: (signed)	Received by (signed)	Date	Time
1				
2				
3				

SHIPPING DETAILS

Delivered to Shipper by: ____________

Method of Shipment: ____________ Airbill # ____________

Received for Lab: ____________ Signed ____________ Date/Time ____________

Enseco Project No ____________

White and Pink Copies to Lab Yellow to Sampler

SS-001

Figure 6-6 Sample Chain of Custody Record

collected and any other pertinent information such as weather conditions, site visitors, ease/difficulty of retrieving samples, etc. All entries will be signed and dated. All members of the of the sampling team will use this notebook. The notebook will be kept as a permanent record.

6.4 Sampling Procedures - GAC Treatment System

Chain-of-custody forms will be completed and all samples shipped to RMAL's laboratory by overnight delivery on the same day they are collected.

Sampling points will be flushed for at least five minutes before collecting a sample. Each PAH sample and matrix spike sample will be collected in six one-liter amber glass bottles, which should be filled and capped in succession. PAH sample bottles will not be rinsed before being filled. The lids of all sample bottles will be taped using plastic adhesive tape after they are capped.

The GAC treated water samples will have to be collected from two sample taps -- one for each column (see Figure 6-7). This will be done by filling three one-liter bottles from the first column sample tap and then three more bottles from the second (six from each for duplicate samples). No notations distinguishing the two taps will be made on the labels. Only four PAH bottles will be extracted and the extracts composited for analysis.

Field blank samples will be prepared by transferring contaminant-free deionized water provided by RMAL into sample bottles in a fashion as closely similar to actual sample collection as possible. Field blank sample bottles will be filled, capped and taped in succession with individual bottles open to the atmosphere for an equal time as for actual process samples. Field blanks will be prepared in the area in which GAC treated water samples are collected.

Field duplicate and matrix spike duplicate samples will be obtained by filling twelve 1-liter bottles at the sampling point by the procedure described above, splitting these into two groups of six bottles, and assigning a different sample number to each of the resulting six-bottle samples. All samples will be packed, cooled to a temperature less than $4^{o}C$, and shipped on the day they are collected.

The sampling team must recognize that great care is required to collect samples for part-per-trillion-level PAH analyses that are free from outside contamination. PAH compounds are present in cigarette smoke, engine exhaust and many petroleum derived oils, among other sources. There will be no smoking anywhere in the GAC treatment building for at least 72 hours prior to the day on which PAH samples are to be collected. Similarly, no vehicles will enter the GAC treatment building and the large access door will stay closed for at least 72 hours prior to the sampling day. Disposable gloves will be worn when collecting, handling and packaging samples. Sample bottles will remain in closed shipping coolers until they are needed, and will be packaged and sealed for shipment as soon as possible after sampling.

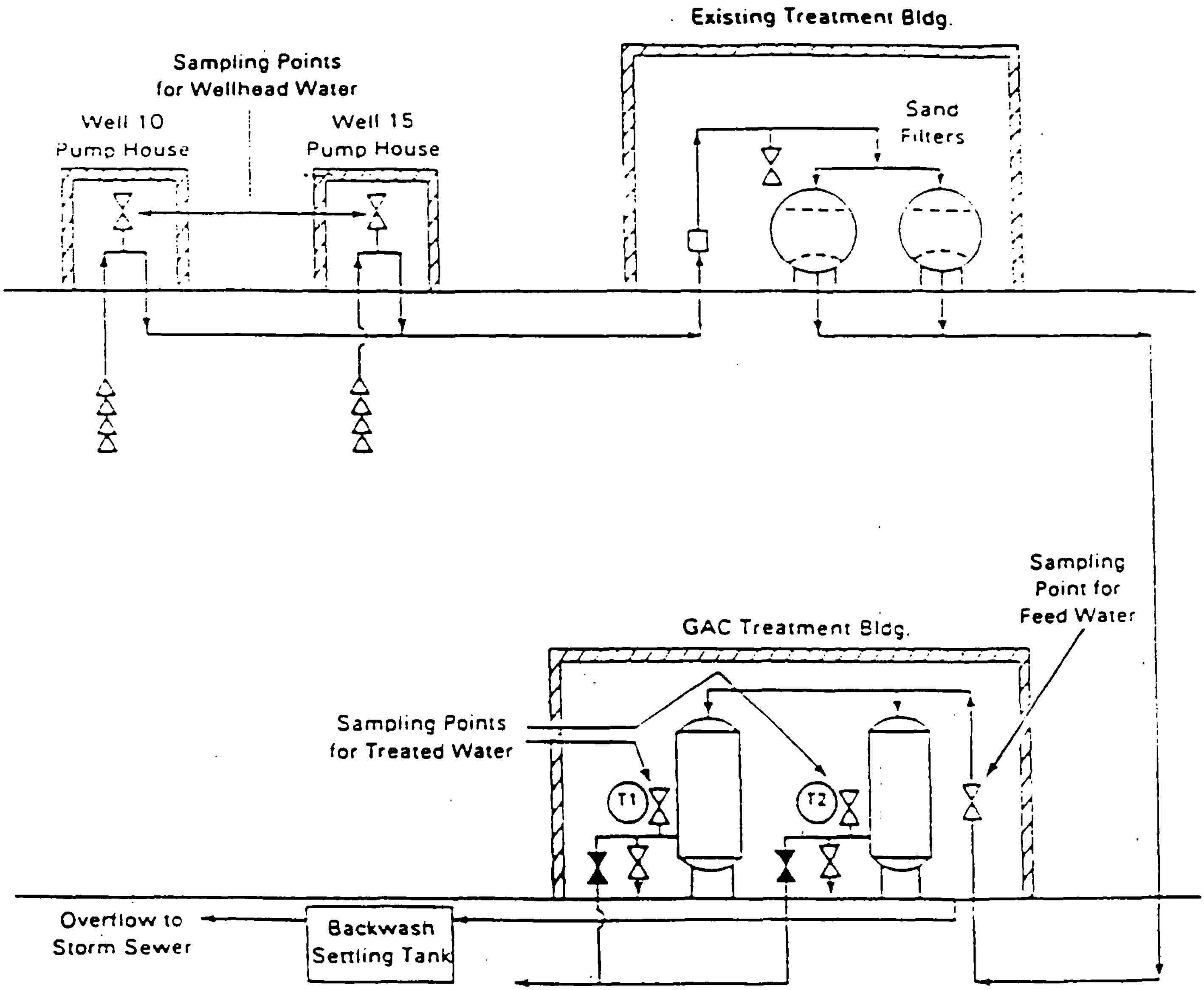

Figure 6-7 Sampling Locations

6.5 Ground water Sampling and Water Level Measurements

Ground water samples will be collected and water level measured in accordance with the procedures outlined in this QAPP. The wells involved in the monitoring program include municipal and commercial wells, piezometers and groundwater monitoring wells (see Table 6-3). Sampling procedures to accommodate the dimensions and configuration of each type of well are described below. Further details on well dimensions, water level measurements and sample acquisition strategies are given in the Site Management Plan.

The importance of proper sampling of wells cannot be over-emphasized. Even though the well being sampled may be correctly located and constructed, special precautions must be taken to ensure that the sample taken from that well is representative of the ground water at that location and that the sample is neither altered nor contaminated by the sampling and handling procedure. Sample collection will always proceed from the less contaminated sampling points to the monitoring points containing progressively higher concentrations of PAH or phenolics.

6.5.1 Decontamination

The field decontamination procedure to be used on sampling equipment which comes into contact with groundwater samples is as follows:

- o disassemble equipment, if applicable,
- o high pressure, hot water steam clean, using potable water.

The laboratory decontamination procedure to be used on sampling equipment which comes into contact with groundwater samples is as follows:

- o disassemble equipment
- o rinse with methanol
- o scrub with hot soapy water
- o rinse three times with hot deionized water
- o set on aluminum foil, dull side up, air dry
- o bake for one hour at 200^{0} C
- o wrap with aluminum foil, dull side in

6.5.2 Field Blanks

Field blank samples will be prepared by transferring contaminant-free deionized water, provided by RMAL, into sample bottles in a fashion as closely similar to actual sample collection as possible. This will involve collecting samples through any non-dedicated sample equipment that is decontaminated between samples. Field blank sample bottles will be filled, capped and taped in succession with individual bottles open to the atmosphere for an equal time as for actual process samples. Field blanks will be prepared in the area where samples are being collected at a rate of one per day or where more than ten samples are collected in a day at a rate of one field blank per ten samples.

6.5.3 Sample Containers (See Table 6-5)

For PAH and phenolics, 1 liter amber glass bottles will be used. Caps will be fitted with pre-cleaned teflon liners. Six bottles are required for each Low-Level PAH sample collected and two bottles for each Non-Criteria PAH and Extended Analysis sample collected. One 16 ounce glass bottle with 2 milliliters of 50 percent sulfuric acid is required for total phenolics. An independent commercial firm shall provide precleaned bottles to RMAL for use on this project.

In the event RMAL is required to prepare bottles for sampling, the bottles will be prepared as follows:

1. Wash bottles with hot detergent water.

2. Rinse thoroughly with tap water followed by three or more rinses with organic-free water.

3. Rinse with Burdick & Jackson quality redistilled acetone, followed by equivalent quality methylene chloride.

4. Allow to air dry in a contaminant free area.

5. Caps and liners must be washed and rinsed also.

   Bottles should be stored and shipped with the Teflon-lined caps securely fastened.

6.5.4 Sample Collection - Monitoring Wells and Piezometers

Because unanticipated or changed conditions may cause difficulty in purging the monitoring wells and piezometers, flexibility in the approach to the method of well purging is necessary. This QAPP proposes that the sampling team be given latitude in the selection of purge equipment necessary to complete the task (various pumping equipment and procedures that may be used for purging monitoring wells are described in SOP 7130 and MPCA's "Procedure

TABLE 6-5
SAMPLE CONTAINERS, PRESERVATION PROCEDURES, AND
MAXIMUM HOLDING TIMES

Parameter	Containers[1]	Preservation[2]	Maximum Holding Time[3]
Water:			
PAH (PPT)	Six 1-liter amber glass bottles, Teflon-lined caps	cool, to 4°C; protect from light	5 days (until extraction), 40 days after extraction
PAH (PPB)	One 1-liter amber glass bottle, Teflon-lined caps	cool, to 4°C, protect from light	5 days (until extraction), 40 days after extraction
Phenolics (Acid Fraction)	One 1-liter amber glass bottle,	cool, to 4°C	5 days (until extraction), 40 days after extraction
Phenolics (Total	One 16 oz. clear glass bottle	cool, to 4°C 2 ml 50% H_2SO_4	28 days

Ref: Federal Register Guidelines/Vol.49, No.209/Friday, October 26, 1984/p. 43260.

1 Matrix spike samples shall consist of the same matrix being analyzed, therefore triple the normal volume when a related matrix spike sample and matrix spike duplicate are to be retrieved.

2 Sample preservation will be performed immediately upon sample collection.

3 Samples will be analyzed as soon as possible after validated time of sample receipt (VTSR). The times listed are the maximum times that samples may be held before analysis and still be considered valid.

for Ground Water Monitoring"; Apprendix A). In all cases where no dedicated pump exists, samples will be retrieved using laboratory - cleaned, stainless steel or teflon bailers as described below.

Table 6-3 specifies that Prairie du Chien-Jordan Aquifer monitor well W70 be monitored. In addition, St. Peter Aquifer monitor wells W24 and W33 may be monitored. Each well is equipped with a dedicated submersible pump and it will be the responsibility of the sampling team to determine if the pump is operable. In the event the dedicated pump within any individual well is operable, well purging and sample retrieval tasks will be completed with the aid of the pump in conformance with monitoring parameters established herein. In the event the dedicated pump within any individual well is inoperable, the pump will be removed and purging/sampling procedures will be as established below.

Monitoring wells and piezometers not equipped with dedicated submersible pumps will be purged using a nondedicated submersible pump, suction pump or bailer. During the purging of each well, temperature, pH and specific conductance of the purge water will be monitored using a Hydrolab water quality monitor (or equivalent). Readings will be taken once per well volume. Stabilization of these readings will indicate that purging is complete and sampling may commence. Upon completion of well purging, samples will be collected from each well using a stainless steel or teflon bailer and a new length of nylon or polyester rope. All nondedicated purging and sampling equipment will be decontaminated before use and between sampling points as described in Section 6.5.1.

Samples will be collected by filling each of the appropriate sample containers in rapid succession, without prerinsing the containers with sample. The bottle will be held under the sample stream without allowing the mouth of the bottle to come in contact with the bailer and filled completely, and the cap securely tightened. All sample labels will be checked for completeness, sample custody forms completed and a description of the sampling event recorded in the field notebook.

6.5.5 Sample Collection - Pumping Wells

At active pumping wells the sampling team will first determine that the wells have actually been pumping during the period preceding sampling. This information may be derived from inspecting flow recorders or from interviewing knowledgeable persons regarding the wells (water department employees, well owners, etc.). The information will be documented in the field notes of the sampling team.

Water level measurements will then be made, if practical. The normal operation of the well will not be interrupted for the purpose of measuring water levels. An electric tape will be used to measure water levels in pumping wells. Sampling will proceed by filling the required containers with water from the sampling tap as near to the well head as possible, and before any holding tanks or treatment is encountered.

If it can not be determined that a well has been pumping at some time during the 24 hour period preceding sampling, or if it is known the well was not pumping, then the well shall be purged until field measurements of temperature, pH, and specific conductance have stabilized after at least three well volumes have been removed from the well. These measurements, water levels, and the amount of water pumped will be recorded in the field notes.

6.6 Sample Preservation, Shipment and Storage

Packaging and shipment of samples shall be in accordance with SOP 7510 (Appendix A). The samples will be iced or refrigerated at 4^oC from the time of collection until extraction. PAH's are known to be light sensitive; therefore, samples will be stored in amber bottles and kept away from prolonged exposure to light. All samples for gas chromatography mass spectrometry (GC/MS) analysis will be extracted within five days of validated time of sample receipt as per CLP SOW 2/88. The analysis will be completed within 40 days following extraction. The holding time for total phenolics is 28 days from sample collection to analysis.

Samples will be protected from breakage and shipped in coolers at a temperature of 4^oC or less. An overnight carrier will be selected to insure delivery at the laboratory within 24-36 hours after collection.

Samples received at the laboratory will be checked for leakage and a notation made regarding sample temperature at time of receipt. All samples should be stored in an organic-free refrigerator at 4^oC.

6.7 Field Measurement Equipment

All field measurement equipment will be controlled to ensure that measurements obtained are accurate and defensible. Table 6-6 summarizes the parameters to be monitored, the instruments to be used for each measurement, procedures including calibration and frequency, and quality control criteria (also refer to Appendix A, SOP 7320, Calibration and Operation of Hydrolab Water Quality Monitor).

In addition, these measurement devices will be issued through a formal equipment tracking system and operated by trained personnel.

TABLE 6-6
FIELD MEASUREMENT EQUIPMENT QUALITY CONTROL

Device	Calibration	Routine Check Method	Routine Check Frequency	Control Limits
pH Meter (Hydrolab)	Standardize in three or more standard buffer solutions	Calibration check-analyze standard buffer solution	After every sample	±0.1 pH units
		Analyze duplicates	After every sample	±0.1 pH units
Conductivity Meter (Hydrolab)	Standardize using two or more KCL solutions	Calibration check-analyze standard KCL solution	1/10 samples	±1% of range being used
		Analyze duplicates	1/10 samples	±1% of range being used
NBS* Thermometer	Factory calibrated	Not required	Not required	±0.1° C
Water Level Measurement Device (Electric)	Factory calibrated	Not required	Not required	±0.01 Ft.

* NBS - National Bureau of Standards

6.8 Duplicate Samples

Duplicate samples will be collected by alternately filling sample bottles from the source being sampled. For six liter sample collection one bottle will be filled for the sample, then one bottle for the duplicate, then a second bottle for the sample and then a second bottle for the duplicate, etc. Duplicates will be taken for each analysis type and each sample type, at a rate of one duplicate sample being collected for each ten samples, with a minimum of one duplicate for any sample batch. There are two sample types for this program: GAC treatment system water and ground water.

For purposes of fulfilling the 10% duplicate requirement, all the sampling points shown on Table 6-3 are the same sample type and have been chosen to maximize the frequency of sample duplication from pumping wells and monitor wells where experience indicates sampling is easiest, thereby insuring consistency of results.

8. CALIBRATION PROCEDURES

Calibration is required to ensure that field and laboratory analytical systems are operating correctly and functioning at the proper sensitivity to meet established detection limits. For this project, calibration is required for field measurements of temperature, pH, and specific conductance. Appendix A contains SOP 7320 that describes calibration procedures for field measurement instruments. This project also requires calibration for the four laboratory analyses (Low-Level, Non-Criteria, Extended, Phenolics). These four analyses are defined in Section 9 of this QAPP.

The specific calibration requirements for each of these analyses are summarized in the subsections below.

8.1 Low-Level (ppt) Analysis

The calibration requirements are described in detail in the Standard Operating Procedure for ppt PAH analyses (Appendix B). The discussion below highlights the key aspects of the calibration requirements.

Prior to use of the method for low level analysis of PAH, a five-point response factor calibration curve must be established showing the linear range of the analysis.

A midpoint calibration standard is analyzed at the start of each 12 hour calibration sequence and the area of the primary characteristic ion is tabulated against concentration for each compound. The response factor (RF) for each compound listed in Table 8-1 is calculated.

These daily response factors for each compound must be compared to the initial calibration curve. If the daily response factors are within ±30 percent of the corresponding calibration curve value the analysis may proceed. If, for any analyte, the daily response factor is not within ±30 percent of the corresponding calibration curve value, the system is out of control and corrective action must be performed.

The quantitation mass ion, which represents the 100% abundance ion, is selected for quantitation and for the daily response factor measurement. The second ion, or confirmation ion, is used for confirmation of the identification. The daily response factor for the quantitation mass ion is compared to the initial calibration curve. During the analysis of the daily calibration standard the percent abundance of the confirmation ion is obtained. This percent abundance is used for identification purposes for samples analyzed during that day. The percent abundance values shown in Table 8-1 are typical values.

TABLE 8-1 TARGET COMPOUNDS AND KEY IONS
FOR LOW LEVEL PAH ANALYSES

CAS NO.	COMPOUND	QUANTITATION MASS ION	CONFIRMATION ION (% ABUNDANCE)
271-89-6	2,3-Benzofuran	118	90 (52)
496-11-7	2,3-Dihydroindene	117	118 (57)
95-13-6	1H-Indene	116	115 (108)
91-20-3	Naphthalene	128	102 (7)
4565-32-6	Benzo(B)Thiophene	134	89 (8)
91-22-5	Quinoline*	129	102 (20)
120-72-9	1H-Indole	117	90 (31)
91-57-6	2-Methylnaphthalene	141	115 (31)
90-12-0	1-Methylnaphthalene	141	115 (28)
92-52-4	Biphenyl	154	153 (35)
208-96-8	Acenaphthylene	152	151 (17)
83-32-9	Acenaphthene	154	153 (93)
132-64-9	Dibenzofuran	168	139 (40)
86-73-7	Fluorene	166	165 (90)
132-65-0	Dibenzothiophene	184	139 (19)
85-01-8	Phenanthrene	178	176 (19)
120-12-7	Anthracene	178	176 (19)
260-94-6	Acridine	179	178 (26)
86-74-8	Carbazole	167	166 (28)
206-44-0	Fluoranthene	202	200 (17)
129-00-0	Pyrene	202	200 (18)
56-55-3	Benzo(A)Anthracene*	228	226 (22)
218-01-9	Chrysene*	228	226 (26)
205-99-2	Benzo(B)Fluoranthene*	252	250 (22)
207-08-9	Benzo(K)Fluoranthene	252	250 (22)
192-97-2	Benzo(E)Pyrene	252	250 (35)
50-32-8	Benzo(A)Pyrene*	252	250 (26)
198-55-0	Perylene	252	250 (24)
193-39-5	Indeno (1,2,3-CD)Pyrene*	276	274 (25)
53-70-3	Dibenz(A,H)Anthracene*	278	279 (20)
191-24-2	Benzo(G,H,I)Perylene*	276	274 (25)
205-82-3	Benzo(J)Fluoranthene*	252	250 (22)

NOTE: The % abundance for the confirmation ion is a <u>typical</u> value. Although these ratios will vary, the relative intensities of confirmation ions must agree within plus or minus 20% between the calibration standard for any given day and the samples run on that day.

* Carcinogenic PAH as defined in Appendix A of the RAP.

Mass tuning will be performed using the mass calibration compound FC43. Tuning will be performed to maximize the sensitivity of the mass spectrometer for the mass range of compounds being analyzed. In the FC43 spectra, the ion abundance of masses 131 and 219 are adjusted to a ratio of 1:1. These two ions are then maximized to be approximately 50 to 70% of the ion abundance of the base mass 69. This procedure maximizes the sensitivity of the instrument in the mass region of interest for the PAH analysis.

The requirements above will be employed for all compounds in Table 8-1 with the exception of benzo(j)fluoranthene. Laboratory studies have shown that Benzo(j)fluoranthene will coelute with either Benzo(b)fluoranthene or Benzo(k)fluoranthene depending on the relative concentration of these two compounds in solution. Benzo(j)fluoranthene cannot be consistantly separated by this method. Therefore if present, it will be detected and reported as Benzo(b) and/or Benzo(k)fluoranthene.

8.2 Non-Criteria Analysis

All Non-Criteria analyses will follow the calibration requirements described in the Contract Laboratory Program Statement of Work for semivolatiles (CLP SOW) dated 2/88. In summary, the SOW requires an initial verification that the mass spectrometer is tuned properly using decafluorotriphenyl phosphine (DFTPP). The SOW also requires an initial five-point calibration be performed for all compounds and that this calibration be verified by the analysis of a daily calibration standard.

The calibration requirements in the SOW are based on the determination of a diverse list of semivolatile organics. Calibration is verified on a daily basis by comparing the responses of a few select compounds, termed calibration check compounds (CCC). Only one of these compounds (acenaphthene) is a target PAH for this project. The response of another group of compounds, termed system performance check compounds (SPCC) are used to verify the analytical system is working properly. None of the SPCCs are target PAH for this project. Finally, the target PAH for this project contain compounds not measured under CLP protocols.

Accordingly, the procedures is the SOW for calibration have been modified to accommodate the differences in the monitoring lists. A calibration standard containing all of the analytes shown in Table 8-1 is used for both initial and continuing calibration in place of the CLP standard. The daily calibration is verified by comparing the response of all 32 compounds (not just a select few) to the response from the initial calibrations. The relative standard deviation (RSD) for <u>each</u> compound must be less than 30% or the system is out of control and corrective action must be performed.

The control limit for the daily calibration is based on the accuracy and precision objectives of this project and experience with this group of analytes. The limits in the CLP SOW, which is slightly more stringent, is based on a select group of compounds with extensive method performance data.

8.3 Extended Analysis

In addition to the compounds listed in Table 8-1, the compounds shown in Table 8-2 are required to be determined in the extended monitoring program. This extended list of compounds include phenols and other PAHs specified for this project.

Analyses for the extended list of compounds will be performed on the semivolatiles extract prepared as described in the CLP SOW.

Since most of the compounds on the extended monitoring list are also target compounds in the CLP protocol, the CLP calibration protocol will be followed.

The system is tuned with DFTPP and calibrated with the semivolatile compounds as specified in the CLP SOW. The compounds used to assess system performance and to verify the continuing calibration (SPCCs and CCCs) are used to verify that the system is in control. The control limits in the SOW are used. In addition, a separate calibration standard containing the PAH in Table 8-2 is used to establish response factors for these compounds.

The absolute and relative retention times, quantitation ions and the internal standards to be used for quantitation for 7,12-dimethylbenz(a)anthracene and 3-methylcholanthrene are listed in Table 8-3.

8.4 Phenolics

A three-point calibration curve covering the linear range of the method will be analyzed prior to the analysis of any samples and with a minimal frequency of once per 12 hours.

TABLE 8-2
TARGET COMPOUNDS FOR EXTENDED ANALYSES

CAS NO.	A. OTHER CARCINOGENIC PAH	REPORTING LIMIT ng/L
195-19-7	Benzo(c)phenanthrene/1	--
215-58-7	Dibenz(a,c)anthracene/2	1.6
192-65-4	Dibenzo(a,e)pyrene/1	--
189-64-0	Dibenzo(a,h)pyrene/1	--
189-55-9	Dibenzo(a,i)pyrene/1	--
57-97-6	7,12-Dimethylbenz(a)anthracene	2.8
56-49-5	3-Methylcholanthrene	3.5

/1 No analytical standards are available.

/2 Coelutes with dibenz(a,h)anthracene. If these isomers are detected, they will be reported as a total value.

CAS NO.	B. ACIDIC COMPOUNDS LISTED IN EPA METHOD 625	REPORTING LIMIT ug/L
108-95-2	Phenol	10
95-57-8	2-Chlorophenol	10
88-75-5	2-Nitrophenol	10
105-67-9	2,4-Dimethylphenol	10
120-83-2	2,4-Dichlorophenol	10
59-50-7	4-Chloro-3-methylphenol	10
88-06-2	2,4,6-Trichlorophenol	10
51-28-5	2,4-Dinitrophenol	50
100-02-7	4-Nitrophenol	50
534-52-1	4,6-Dinitro-2-methylphenol	50
87-86-5	Pentachlorophenol	50

TABLE 8-3

RETENTION TIMES, QUANTITATION IONS AND INTERNAL STANDARDS FOR EXTENDED PAH LIST

Compound	Absolute Retention Time	Relative Retention Time	Quantitation Ions	Internal Standard
7,12-dimethylbenz(a) anthracene	30:51:00 minutes	0.890 minutes	M/Z 256	D_{12}-B(A)P[1] M/Z 264
3-methylcholanthrene	32:48:50 minutes	1.085 minutes	M/Z 268	D_{12}-B(A)P[1] M/Z 264

[1] Benzo(A)Pyrene

9. ANALYTICAL PROCEDURES

9.1 Low-Level Analysis

As specified in the Consent Decree, four types of analyses are to be performed as part of the RAP for this project. These four analyses are defined below, and the details of the specific analytical procedures are presented in subsequent subsections.

- Low-Level: Refers to the determination of a specific list of 21 polynuclear aromatic hydrocarbons using GC/MS with operation in the selected ion monitoring (SIM) mode. The list of target PAH contains carcinogenic and non-carcinogenic compounds and is shown in Table 8-1 of the QAPP. The list includes 14 compounds which are not on EPA's priority pollutant, Appendix IX or Superfund target compound list. The analytical methodology is based on well known principles of GC/MS technology. Although there is no EPA method that embodies this technique for this class of compounds, methods developed for the measurement of polychlorinated dibenzodioxins (e.g., Methods 613 and 8280) are based on selected ion monitoring technology.

- Non-Criteria: The Low-Level PAH method is designed to measure PAH at the sub-ppb level. At higher concentrations, the compounds can be measured under scanning GC/MS conditions. Since scanning GC/MS provides more reliable qualitative data, this method, termed "Non-Criteria PAH" is preferred for samples containing ppb concentrations of PAH. The method is based on the Contract Laboratory Program (CLP) protocol for semivolatile organics with the appropriate modifications to address the differences in the monitoring lists.

- Extended: Some samples are analyzed for the specific list of compounds shown in Table 8-2 of the QAPP using scanning GC/MS. This list, termed "extended" analyses, includes additional PAH, specific acid (phenolic) compounds and a provision for "identifying" unknown compounds. Unknown compounds will be identified and reported from the analysis of the acid fraction only. As in the Non-Criteria analyses, analyses are performed using CLP protocols with the appropriate modifications.

- Phenolics: Refers to the determination of "total phenols" using a colorimetric procedure.

A method has been developed for the analysis of selected target PAH and heterocycle compounds at the part per trillion level (ppt, ng/L) in water. The analysis is carried out by isolation of the target analytes by liquid-liquid extraction of the water sample with an organic solvent. Quantitation of the isolated target analytes is performed by gas chromatography/mass spectrometry (GC/MS) in the selected ion monitoring mode (SIM). The method is generally applicable for the measurement of any PAH or related compound. For this project, only those compounds listed in Table 8-1 will be determined.

In summary, a measured volume of sample is extracted with methylene chloride. Analysis of the concentrated extract is performed by gas chromatography/mass spectrometry using the selected ion monitoring scanning mode under electron impact ionization conditions. Specific details of this methodology can be found in Appendix B, Determination of Low-Level (Part Per Trillion) PAH and Heterocycles in Water. This method is designed to analyze samples containing up to 600 ppt of an individual PAH. With dilution of the sample extract, the effective range of the method can be extended into the ppb range. However, sample dilutions may result in loss of information concerning recovery of surrogates. For this reason, an optional sample preparation technique is contained in the method. This optional technique can be used if historical information indicates that the target compounds are present in concentrations in excess of 600 ppt.

9.2 Non-Criteria Analysis

The selected target PAH and heterocycle compounds listed in Table 8-1 can be determined by GC/MS in the scanning mode at the ppb and higher concentrations. This analysis, termed Non-Criteria analysis, uses the methodology contained in the Contract Laboratory Program Statement of Work for semivolatiles dated 2/88 (CLP SOW). The only deviations from this SOW are as follows:

1. The calibration is performed as set forth in Section 8 of this QAPP.
2. The internal QC checks are set forth in Section 11 of this QAPP.
3. Data are reported only for those compounds listed in Table 8-1.

9.3 Extended Analysis

The target compounds listed in Table 8-2 are measured using the methodology contained in the Contract Laboratory Program Statement of Work (CLP SOW) for semivolatile organic dated 2/88. The only deviations from this SOW are as follows:

1. The calibration is performed as described in Section 8 of the QAPP.
2. The only target compound in the analytical reports are those listed in Table 8-2.

9.4 Phenolics

Total phenolics will be determined by RMAL SOP No. 1112 which references Methods 420.1 and 420.2 as published in the "Methods for Chemical Analysis for Water and Waste, EPA 600/4-79-020" (refer to Appendix B).

10. DATA REDUCTION, VALIDATION AND REPORTING

10.1 Data Reduction and Validation

All project data will be subjected to a three-tier process including review by operations, by the data review groups for inorganics and GC/MS and the final review by the Project Coordinator prior to its release. The review process has been developed to minimize errors associated with sample processing, sample analysis and data reporting and to ensure that information pertaining to a given sample is well documented.

Appendix A contains Standard Operating Procedures (SOP's) for laboratory data review. Refer to SOP No. LP-RMA-0002 for information relative to review policies and processes. In addition, the SOP's for the analytical methods contain the calculation techniques required to obtain reportable concentrations from the raw data.

10.2 Turnaround Time

In accordance with Section 3.2 of the RAP, RMAL has agreed to a 30 working day turnaround. The City, however, makes no enforceable commitment under the RAP except for a maximum of 5 days from validated time of sample receipt for extraction of organics and 40 days following extraction for analysis of organics. For non-organic analyses, the City makes no enforceable commitment under the RAP except to meet the recommended maximum analytical holding times.

10.3 Reporting/Data Deliverables

RMAL shall prepare summary reports and data packages in a format that mimics the format described in Exhibit B of Organic SOW 2/88 for the Contract Laboratory Program. Specifically, Form I, SV-1 and SV-2 in Exhibit B of the CLP SOW will be changed to include the PAH list of parameters shown in Table 8-1 of the QAPP. Form II, SV-1 will show the surrogates for the PAH analysis. Form III, SV-1 will show the spike compounds for the PAH analyses. Form VI, SV-1 and SV-2 and Form VII, SV-1 and SV-2 will be altered to show just the target parameters shown in Table 8-1 of the QAPP. Finally, Form VIII, SV-1 and SV-2 will be modified to show the internal standards for the PAH method. In addition, in the Low-Level PAH analyses, compounds which are determined to be present in the samples based on careful inspection of the data, but which do not meet the secondary ion confirmation criteria will be flagged with an asterisk (*). The reporting forms in Exhibit B will be modified to show the target lists of parameters, surrogates and spiking compounds for the Low-Level PAH.

RMAL has determined the method detection limits for the part per trillion PAH analysis of water samples, utilizing GC/MS selected ion monitoring, according to the method described in Appendix B to Part 136 of the Friday, October 26, 1984 Federal Register, Vol. 49, No. 209 - Definition and Procedure for the Determination of the Method Detection - Revision 11.1. Table 10-1 lists the compounds, the observed concentrations of seven replicates spiked at 5 parts per trillion, the standard deviations and the method detection limits. RMAL has also determined the method detection limits for part per billion Phenolics according to Method 420.2 as published in the "Methods for Chemical Analysis for Water and Waste, EPA 600/4-79-020" (see Table 10-2).

These calculated method detection limits will be used in sample reporting as follows:

- Analytes detected at concentrations greater than or equal to the calculated method detection limits will be reported with no qualifiers.

- Analytes which are not detected will be reported as the calculated detection limit followed by a "U" qualifier which is used in the EPA Contract Lab Program (CLP) to indicate a non-detected compound.

- Analytes that are detected at concentrations less than the calculated method detection limits will be reported followed by a "J" qualifier which is used in the EPA Contract Lab Program (CLP) to indicate that a reported value is below the method detection limit.

The various items in the data package are listed below:

- Sample Traffic Reports or Chain-of-Custody
- Sample Data Summary Report Including:
    - Case narrative
    - Tabulated target compound results by fraction
    - Surrogate spike analysis results by fraction
    - Matrix spike/matrix spike duplicate results by fraction
    - Blank data by fraction
- Sample Data Package including:
    - Case narrative
    - Traffic reports
    - Raw data

The City will present reports in a manner consistent with the requirements of the RAP. In addition, data packages containing all elements listed above will be presented for the sample analyses completed, if so directed by the EPA. The EPA shall be responsible for identifying the specific sample analyses for which data packages will be provided.

TABLE 10-1
METHOD DETECTION LIMIT REPORT

Compound	Sample #1	Sample #2	Sample #3	Sample #4	Sample #5	Sample #6	Sample #7	Standard Deviation	Method Detection Limit (3a) *
2,3-Benzofuran	19.4*	20.9*	18.0*	19.5*	20.3*	21.5*	16.6*	1.70*	5.1*
2,3-Dihydroindene	4.3	4.2	4.7	3.7	3.8	4.9	4.7	0.46	1.4
1H-Indene	4.4	4.2	4.6	3.9	4.1	4.7	4.6	0.30	0.9
Naphthalene	20.5*	21.0*	18.5*	20.3*	23.0*	23.5*	17.6*	2.15*	6.5*
Benzo(B)thiophene	3.6	3.5	3.9	3.4	3.3	3.8	4.1	0.29	0.9
Quinoline	4.7	4.0	4.1	3.7	3.3	4.4	4.1	0.45	1.4
1H-Indole	3.7	4.5	5.6	3.2	3.2	4.2	4.0	0.84	2.5
2-Methylnaphthalene	5.4	5.0	5.3	5.1	4.8	4.9	5.7	0.31	0.9
1-Methylnaphthalene	4.5	4.2	4.6	3.8	3.7	4.7	5.2	0.53	1.6
Biphenyl	17.9*	18.1*	16.4*	18.4*	18.1*	19.3*	15.0*	1.43*	4.3*
Acenaphthylene	3.9	3.6	4.6	3.7	3.5	4.4	4.5	0.46	1.4
Acenaphthene	4.2	3.7	4.7	3.5	3.5	4.1	4.1	0.43	1.3
Dibenzofuran	4.3	3.9	4.6	4.1	3.7	4.6	4.2	0.34	1.0
Fluorene	4.4	4.0	4.5	4.0	4.0	4.6	4.8	0.33	1.0
Dibenzothiophene	4.0	3.5	4.0	3.5	3.2	3.9	4.2	0.36	1.1
Phenanthrene	4.7	3.9	4.7	3.9	3.6	4.2	4.5	0.43	1.3
Anthracene	4.5	3.8	4.5	4.1	3.6	4.1	4.6	0.38	1.1
Acridine	4.1	4.3	4.9	4.1	3.8	2.4	2.3	0.98	2.9
Carbazole	4.5	3.2	4.8	3.5	3.9	3.1	3.8	0.64	1.9
Fluoranthene	4.5	3.8	4.7	3.9	3.6	4.4	4.7	0.45	1.4
Pyrene	4.3	3.7	4.4	3.9	3.4	4.2	4.7	0.45	1.4
Benzo(A)anthracene	4.6	3.6	4.0	3.6	3.3	5.3	5.3	0.83	2.5
Chrysene	4.3	3.3	3.7	3.3	2.9	5.1	5.3	0.94	2.8
Benzo(B)fluoranthrene	4.6	3.4	3.8	3.6	2.8	4.9	5.0	0.83	2.5
Benzo(K)fluoranthrene	4.1	3.2	3.5	3.2	3.2	4.9	4.8	0.76	2.3
Benzo(E)pyrene	4.9	3.8	4.1	3.3	3.5	4.9	4.4	0.64	1.9
Benzo(A)pyrene	4.5	3.2	3.8	3.2	2.9	4.8	4.5	0.76	2.3
Perylene	4.6	3.6	3.8	3.5	3.3	5.3	5.1	0.82	2.5
Indeno(1,2,3-CD)pyrene	4.5	3.4	3.4	2.9	3.0	4.5	4.2	0.69	2.1
Dibenz(A,H)anthracene **	4.2	3.5	3.6	3.1	3.3	4.6	4.1	0.54	1.6
Benzo(G,H,I)perylene	3.8	3.0	2.9	2.6	2.9	4.9	4.7	0.94	2.8

Note: Amount spiked = 5 ng/L.

* Data for 2,3-Benzofuran, Naphthalene and Biphenyl were obtained from previous detection limit study. Spike levels = 20 ng/L.

** Compounds co-elute

TABLE 10-2

METHOD DETECTION LIMIT STUDY - TOTAL PHENOLICS

Sample #	Concentration Detected (mg/L)
1	0.0315
2	0.0340
3	0.0291
4	0.0315
5	0.0291
6	0.0291
7	0.0315

Calculated Standard Deviation = 0.0018

Calculated Method Detection Limit = 0.00579 mg/L
= 5.8 ug/L

10.4 Reporting Requirements for Samples Exceeding Advisory Levels or Drinking Water Criterion

For active drinking water wells, RMAL will notify the City of St. Louis Park by telephone, within 24 hours of completing an analysis, whenever a sample analysis is shown to exceed the following Advisory Levels or Drinking Water Criterion:

Parameter	Advisory Level	Drinking Water Criterion
Sum of Benzo(a)pyrene and Dibenz(a,h)anthracene*	3.0 ng/L*	5.6 ng/L
Total Carcinogenic PAH +	15 ng/L**	28 ng/L**
Total Other PAH	175 ng/L	280 ng/L

*Or the detection limit, whichever is largest.

**Different concentrations for additional carcinogenic PAH may be established in accordance with the procedure specified in Part D.1 of the Consent Decree.

+See Table 10-3.

10.5 Final Evidence Files

The final evidence (or data) files will be maintained for the period specified in the RAP. Evidence files will consist of all data necessary to completely reconstruct the analysis, and will consist of (at a minimum): all field documents, logs, project reports, raw data, continuing calibration checks, DFTPP tune, detection limits, chain of custody documentation, quality control data for blanks and matrix spikes, results forms, and a file custodian. In addition, the analytical report, which contains a brief discussion of the method and a more detailed narrative of any analytical issues is included in the package. The City will maintain these files in a secure, limited access area under the custody of the Project Manager. RMAL maintains all GC/MS raw data files on tapes or other magnetic media for an indefinite period. This data will be available upon request.

TABLE 10-3

CARCINOGENIC PAH[a]

benz(a)anthracene
benzo(b)fluoranthene
benzo(j)fluoranthene
benzo(ghi)perylene
benzo(a)pyrene[b]
chrysene
dibenz(a,h)anthracene[b]
indeno(1,2,3-c,d)pyrene
quinoline

(a) The total maximum levels of carcinogenic PAH established in the Consent Decree-RAP are:

Advisory Level - 15 ng/l

Drinking Water Criterion - 28 ng/l

(b) The total maximum levels of the sum of benzo(a)pyrene and debenz(a,h) anthracene are:

Advisory Level - 3.0 ng/l (or the lowest concentration that can be quantified, whichever is greater)

Drinking Water Criterion - 5.6 ng/l

11. INTERNAL QUALITY CONTROL

The internal quality control checks will include field blanks, method blanks, surrogate spikes, duplicate analyses, monitoring of internal standard area, and matrix spike analyses. Each quality control check has a specific level of performance which will be reevaluated in an ongoing basis and amended as appropriate through mutual agreement of the EPA, MPCA, and City. The specific details are presented below.

11.1 Low-Level and Non-Criteria PAH Analyses

Internal quality control checks for the Low-Level and Non-Criteria PAH analyses will consist of method blanks analysis, surrogate compound analysis, matrix spike analysis, analysis of duplicate samples, and monitoring of internal standard areas.

11.1.1 Method Blank Analysis

A method blank consists of deionized, distilled laboratory water carried through the entire analytical scheme (extraction, concentration, and analysis). The method blank volume must be approximately equal to the sample volumes being processed.

Method blank analyses are performed at the rate of one per case*, each 14 calendar day period during which samples in a case are received, with every 20 samples of similar concentration and/or sample matrix, or whenever samples are extracted by the same procedure, whichever is most frequent.

Different control limits have been established relative to method blanks for the Low-Level and Non-Criteria analyses since the target compounds in Table 8-1 are present as "laboratory contaminants" in method blanks at the ppt concentration level.

For the Low-Level analyses, an acceptable method blank analysis must not contain any carcinogenic PAH in Table 8-1 at concentrations greater than or equal to the Method Detection Limits (MDL) in Figure 10-1 or any non-carcinogenic PAH at a concentration greater than 5 times the MDL. For the Non-Criteria analyses, an acceptable method blank does not contain any PAH in Table 8-1 above 10 micrograms per liter. If the method blanks do not meet these criteria, the analytical system is out of control and the source of the contamination must be investigated and corrective measures taken and documented before further sample analysis proceeds.

* A case is a group or a set of samples collected from a particular site over a given period of time.

11.1.2 Surrogate Compound Analysis

As detailed in the SOP (Appendix B), the laboratory will spike all samples and quality control samples with deuterated PAH surrogate compounds. The surrogate compound will be spiked into the sample prior to extraction to measure individual sample matrix effects associated with sample preparation and analysis.

RMAL will take corrective action whenever the surrogate recovery is outside the acceptance criteria shown below. The corrective action is described in Section 15 of this QAPP.

	Acceptance Criteria %	
Surrogate	Low-Level	Non-Criteria
Naphthalene-d8	14-108	25-175
Fluorene-d10	41-162	25-175
Chrysene-d12	10-118	25-175

11.1.3 Matrix Spike/Matrix Spike Duplicate Analysis

Low-Level PAH matrix spike and matrix spike duplicate samples will be analyzed as outlined in the RMAL SOP (Appendix B). Non-Criteria PAH matrix spike and matrix spike duplicate samples will be analyzed pursuant to the criteria of CLP SOW-2/88.

The laboratory will spike and analyze 5% matrix spike and matrix spike duplicate samples. RMAL will spike seven representative compounds into water. These compounds and the spiking levels are listed below:

	PPT	Non-Criteria
Naphthalene	20 ng/L	50 ug/L
Fluorene	20	50
Chrysene	20	50
Indene	20	50
Quinoline	20	50
Benzo(e)pyrene	20	50
2-methyl naphthalene	20	50

The matrix spike criteria for data validity are as follows:

- o The average of the percent recoveries for all compounds must fall between 20 and 150 percent.
- o Only one compound can be below its required minimum percent recovery. These minimum percent recoveries are:
  1) 10% for chrysene
  2) 20% for all other compounds.

Corrective action will be performed if these criteria are not achieved as described in Section 15.

11.1.4 Duplicates

Relative percent difference between duplicates will be calculated for each detected compound per procedures outlined in Section 14.3. of this QAPP.

11.1.5 Internal Standard Areas

The area of the internal standard will be monitored on each analysis. The area from the daily calibration standard will be used to set a daily acceptance criteria. If the internal standard areas in samples changes by more than a factor of two (-50% to + 100%) from the daily standard, corrective action must be performed. Additionally, the retention times of internal standards must agree to +/- 30 seconds of the daily standards.

11.2 Extended Analysis

The internal quality control checks for Extended Analyses will consist of surrogate spikes, matrix spikes, matrix spike duplicates, method blanks, etc. as described in the CLP SOW for semivolatile organics. The acceptance criteria are as defined in the SOW.

11.3 Phenolics

The internal quality control checks for phenolics will mimic those for inorganics in the CLP program and will include the analysis of a method blank, a laboratory check standard, a matrix spike sample, a matrix spike duplicate, and a duplicate sample. The specific details for each of these QC checks are summarized below.

11.3.1 Blanks

A "Preparation Blank" is analyzed with each batch of 20 samples. This blank is carried through the entire procedure, including the distillation step. Additional blanks, termed "Initial Calibration Blank" (ICB) and "Continuing Calibration Blank", (CCB) are also analyzed. These blanks are used only to evaluate the determinative step and are not distilled. They are analyzed at a frequency of one ICB per 20 samples and one CCB per 10 samples.

An acceptable blank must not contain phenolics above the nominal reporting limit of 5 micrograms per liter. If any of the blanks contain phenolics above 5 micrograms per liter, the system is out of control and corrective action must be performed.

11.3.2 Laboratory Check Standard

The calibration is verified by the analysis of two different laboratory check standards. An "Initial Calibration Verification" (ICV) check standard is analyzed at a frequency of one per 20 samples. This check is carried through the entire procedure, including the distillation step. The measured value from this check standard must be between 75% and 125% of the true value.

A "Continuing Calibration Verification" (CCV) check standard is analyzed at a frequency of one per 10 samples. This standard is used to verify the determinative step only. The measured value must be between 85% and 115% of the true value.

If the measured values from the check standards are not within control limits, the system is out of control and corrective action must be performed.

11.3.3. Matrix Spikes/Matrix Spike Duplicates

As for the other tests, matrix spikes and matrix spike duplicates will be performed at a frequency of 5%. The spike level is 50 micrograms per liter. The recovery of the matrix spike must be between 75% and 125%. Corrective action is performed if these criteria are not achieved.

11.3.4 Duplicates

Field duplicate analyses are performed at a frequency of 10%. Corrective action is performed if the relative difference from the duplicate analysis is greater than 70%.

12. PERFORMANCE AND SYSTEM AUDITS

The ability of the Sampling Team to successfully monitor pumping wells and monitor wells, and the ability of the laboratory to successfully analyze groundwater samples will be confirmed by a series of audits conducted in conjunction with the implementation of the groundwater monitoring program established in the Consent Decree-RAP.

12.1 Field Audits

EPA Region 5 Central Regional Laboratory (CRL) and the Central District Office (CDO) are responsible for the external audits of field activities, including field sampling and measurements, for compliance of requirements specified for this project. The Quality Assurance Manager and/or Field Team Leader of ENSR will be responsible for internal audits to see if field sampling and measurements are properly followed.

12.2 Laboratory Audits

RMAL participates in a variety of federal and state certification programs, (including the EPA CLP), that subject the laboratory to stringent systems and performance audits on a regular basis. A <u>system audit</u> is a review of laboratory operations conducted to verify that the laboratory has the necessary facilities, equipment, staff and procedures in place to generate acceptable data. A <u>performance audit</u> verifies the ability of the laboratory to correctly identify and quantitate compounds in blind check samples submitted by the auditing agency. The purpose of these audits is to identify those laboratories that are capable of generating scientifically sound data.

12.2.1 External Audits

RMAL will be subjected to EPA performance and system audits for approval/disapproval specific to the requirements of this program. The Laboratory Scientific Support Section (LSSS) of EPA Region 5 Central Regional Laboratory (CRL) is responsible for the audits.

12.2.2 Internal Audits

In addition to external audits conducted by EPA Region 5 CRL, the City of St. Louis Park and/or Northwest Regional Quality Assurance Manager of ENSR (officed in Fort Collins, Colorado) will be responsible for at least biennial auditing of the RMAL laboratory. Audit procedures will include both system audits and performance audits as necessary to satisfy the City that RMAL is capable of rendering satisfactory laboratory services under this QAPP (see Figure 12-1 for the City of St. Louis Park Audit Checklist).

CITY OF ST. LOUIS PARK AUDIT CHECKLIST

Sample Receiving

YES NO

Are refrigerator/cold storage area temperatures recorded daily and are records properly maintained?
Comments:

Are sample chain-of-custody forms completed properly?
Comments:

Are the temperatures of the coolers being checked and recorded?
Comments:

Are volatile samples stored separately?
Comments:

Is access to sample storage area restricted?
Comments:

Data Review

Are all calculations checked by the analyst for accuracy and completeness?
Comments:

Are anomalies documented and reported?
Comments:

What corrective actions are taken when the analytical results fail to meet QC criteria?
Comments:

Standard Preparation

Are Class 5 weights used to check the balances?
Comments:

Are non-EPA and non-NBS neat materials compared to EPA or NBS whenever possible?
Comments:

Have expired standards and reagents been discarded?
Comments:

Inorganics

Is the conductivity of the Milli-Q water system checked daily and recorded?
Comments:

Is linearity verified (correlation coefficient of at least 0.995) before sample analysis?

Figure 12-1 City of St. Louis Park Audit Checklist

Figure 12-1 (continued)

YES NO

If the CCV does not meet acceptance criteria, is the system recalibrated and are all affected samples reanalyzed?
Comments:

Organic Extraction

Are all reagents and solvents screened for potential contamination?
Comments:

What is the source of reagent water?
Comments:

Are spiking solutions and standards prepared from separate stocks?
Comments:

Is glassware cleaned appropriately?
Comments:

Are the hood airflows checked and how often are they checked?
Comments:

GC/MS Lab

Are current SOP's available for all personnel in the area?
Comments:

Is preventive maintenance performed on all instruments?
Comments:

Have MDL studies been performed on all methods?
Comments:

Are method blanks analyzed with every batch of samples?
Comments:
Are results of QC samples verified to determine if QC criteria has been met before sample analysis begins?
Comments:

Are QC results which are outside of acceptance limits checked for error?
Comments:

Are corrective actions taken as necessary and documented and samples reprepped/reanalyzed?
Comments:

Are logbooks reviewed periodically, as indicated by the signature/date/comments of the reviewer?
Comments:

13. PREVENTIVE MAINTENANCE

Since instrumental methods of analysis require properly maintained and calibrated equipment, the operation and maintenance of modern analytical instrumentation is of primary importance in the production of acceptable data. In order to provide this data, RMAL subscribes to the following programs:

- maintenance agreements/service contracts with instrument manufacturers
- laboratory preventive maintenance program

13.1 Service Contracts

Analytical equipment utilized by RMAL laboratory personnel for this project are covered by maintenance agreements with the instrument manufacturers. These manufacturers provide for both periodic "preventive" service calls as well as the non-routine or emergency calls.

13.2 Instrument Logbooks

Individual instrument logbooks are maintained for each piece of equipment and located near the instrument. General information contained in the logbooks include:

- Inventory information:
  equipment name, model number, serial number, manufacturer, date of acquisition, original cost
- Service tasks and intervals:
  cleaning, calibration, operation based on the manufacturer's recommended schedule, and previous laboratory experience
- Service record:
  date of breakdown, date of return to service, downtime, problems, repairs, cost of repairs, who performed the repairs, parts required, etc.
- calibration/performance checks
- daily operational notes

Analysts are referred to manufacturers' operating manuals for specific procedures to be followed in the operation and/or maintenance of the individual instruments.

Laboratory preventive maintenance includes any tasks that can be performed in-house, i.e., systematic cleaning of component parts as recommended in the instrument manual. If problems cannot be corrected by laboratory personnel, the instrument service representative is contacted and a service call requested to correct the problem.

13.3 Field Equipment

All field equipment shall be inspected daily for damaged or missing pieces, which will be replaced as needed. .

13.3.1 Thermometer

The field workers will handle the thermometer with care to preserve its measurement integrity. After each use, the thermometer will be rinsed with de-ionized or potable water, wiped dry, and returned to its protective case.

13.3.2 Water Level Measurement Tape

Before each use, the battery will be checked using the equipment's element test function, and replaced if necessary. The tape and probe will be wiped clean and rinsed with de-ionized or potable water after each use.

13.3.3 Hydrolab

The hydrolab instrument shall be maintained in accordance with the manufacturer's requirements. In particular, the battery will be checked daily, and replaced if necessary. The instrument shall be operated and stored at temperatures above freezing, to avoid damaging the instrument. After each use, the instrument will be rinsed with potable or de-ionized water, wiped dry and returned to its storage container. The sonde unit must be covered with its protective, water-filled cap.

14. SPECIFIC PROCEDURES TO ASSESS DATA PRECISION, ACCURACY AND COMPLETENESS

A quality control program is a systematic process that controls the validity of analytical results by measuring the accuracy and precision of each method and matrix, developing expected control limits, using these limits to detect errors or out-of-control events, and requiring corrective action techniques to correct, prevent or minimize the recurrence of these events. The quality assessment techniques described below consist of the techniques used to assure that statistical control has been achieved.

The accuracy and precision of sample measurements are influenced by both external and internal factors. External factors or errors are those associated with field collection and sample transportation. Internal factors or errors are those associated with laboratory analysis. External factors are defined briefly in Section 14.1. Internal factors are defined in Section 14.2.

14.1 External Components

The results for quality control samples taken in the field represent the best estimates of accuracy and precision for the samples, since these values reflect the entire process from sample collection through sample analysis. The frequency of these control samples is described in Sections 5 and 6. Below is a brief description of the information provided by each of these control samples:

- Field blank - provides an estimate of bias based on contamination; includes effects associated with sample preservation, shipping, preparation, and analysis.

- Field collected samples or duplicates - independent samples collected at the same point in space and time. These give the best measurement of precision for sample collection through analysis.

14.2 Internal Components

The results of quality control samples created in the laboratory represent estimates of analysis and precision for the preparation and analysis steps of sample handling. This section describes the quality control-type information provided by each of these analytical measurements. The frequency of each of these measurements is discussed in Sections 5 and/or 11.

- Surrogates - provide an estimate of bias based on recovery of similar compounds, but not the compounds analyzed, for each sample, preparation and analysis.

- Internal standard - an analyte that has the same characteristics as the surrogate, but is added to the sample extract just prior to analysis. It measures bias or change in instrument performance from sample to sample, incorporating matrix effects associated with the analysis process only.

- Matrix spikes/Matrix spike duplicates - the matrix spike is added prior to preparation and analysis. The analyte used is the same as that being analyzed and usually is added to a selected few samples in a batch of analyses. It incorporates matrix effects associated with the laboratory analysis.

- Method blanks - provide an estimate of bias based on contamination.

14.3 Calculation Techniques

The quality assessment procedures described above require calculations of relative percent difference (duplicate analyses) and percent recovery (matrix and surrogate spikes). The techniques for performing these calculations are described below.

- Precision - is the degree to which the measurement is reproducible. Precision is assessed by duplicate measurements by calculating the Relative Percent Difference (RPD) between duplicate measurements. The RPD is calculated as follows:

$$RPD = \frac{|D_1 - D_2|}{(D_1 + D_2)/2} \times 100$$

where: RPD = relative percent difference

D_1 = first sample value

D_2 = second sample value (duplicate)

- Accuracy - is a determination of how close the measurement is to the true value.

  The determination of the accuracy of a measurement requires a knowledge of the true or accepted value for the signal being measured. Accuracy may be calculated in terms of percent recovery as follows:

$$\text{Percent Recovery} = \frac{X}{T} \times 100$$

where:

X = the observed value of measurement

T = "true" value

- Completeness - is a measure of the amount of valid data obtained from a measurement system compared with the amount that was expected to be obtained under correct normal conditions.

  To be considered complete, the data set must contain all QC check analyses verifying precision and accuracy for the analytical protocol. In addition, all data are reviewed in terms of stated goals in order to determine if the data base is sufficient.

  When possible, the percent completeness for each set of samples is calculated as follows:

$$\text{Completeness} = \frac{\text{valid data obtained}}{\text{total data planned}} \times 100\%$$

- Comparability - expresses the confidence with which one data set can be compared to another data set measuring the same property. Comparability is ensured through the use of established and approved analytical methods, consistency in the basis of analysis (wet weight, volume, etc.), and consistency in reporting units (ppt, ppb, etc.).

15. CORRECTIVE ACTION

Corrective actions are required whenever an out-of-control event or potential out-of-control event is noted. The investigative action taken is somewhat dependent on the analysis and the event.

Laboratory personnel are alerted that corrective actions may be necessary if:

- o QC data are outside the warning or acceptable windows for precision and accuracy;
- o Blanks contain target analytes above acceptable levels;
- o Undesirable trends are detected in spike recoveries or RPD between duplicates;
- o There are unusual changes in detection limits;
- o Deficiencies are detected by the QA department during internal or external audits or from the results of performance evaluation samples; or
- o Inquiries concerning data quality are received.

Corrective action procedures are often handled at the bench level by the analyst, who reviews the preparation or extraction procedure for possible errors, checks the instrument calibration, spike and calibration mixes, instrument sensitivity, and so on. If the problem persists or cannot be identified, the matter is referred to the laboratory supervisor, manager and/or QA department for further investigation. Once resolved, full documentation of the corrective action procedure is filed with the QA department.

Generally, out-of-control events or potential out-of-control events are noted on an out-of-control event form (see Figure 15-1). This form is part of the data package and, thus, must be completed prior to data approval. If an out-of-control event does occur during analysis, for instance, a surrogate recovery falls out the expected range, the analyst must describe on this form: the event, the investigative and corrective action taken, and the cause of the event, and notify the Laboratory Quality Control Director. In some cases, investigation of an out-of-control event will reveal no problems. In such cases, only the event and the investigative action is recorded. If an out-of-control event is discovered during data package review, the Laboratory Quality Control Director notifies the supervisor for corrective action.

QC Lot ______________________________

Associated Samples ______________________________

PROBLEM: (Briefly decribe problem) ______________

Analyst:
Date:

RESULTS/CONCLUSIONS of the Investigation:

Analyst:
Supervisor:
Date:

CORRECTIVE ACTIONS (including follow-up)

Supervisor:
QA Approval:
Date:

Figure 15-1 Warning/Out-of-Control Form

15.1 Low-Level and Extended PAH Analyses

15.1.1 Surrogates

As discussed in Section 11.1.2, corrective action will be performed whenever the surrogate recovery is outside the following acceptance criteria:

Surrogate	Acceptance Criteria %	
	Low-Level	Non-Criteria
Naphthalene-d8	14-108	25-175
Fluorene-d10	41-162	25-175
Chrysene-d12	10-118	25-175

The following corrective action will be taken when required as stated above:

a) Check calculations to assure there are no errors;

b) Check internal standard and surrogate solutions for degradation, contamination, etc., and check instrument performance;

c) If the upper control limit is exceeded for only one surrogate, and the instrument calibration, surrogate standard concentration, etc. are in control, it can be concluded that an interference specific to the surrogate was present that resulted in the high recovery and this interference would not affect the quantitation of other target compounds. (The presence of this type of interference can be confirmed by evaluating the chromatographic peak shapes and ion intensities of the surrogates.)

d) If the surrogate could not be measured because the sample required a dilution, no corrective action is required. The recovery of the surrogate is recorded as D with the note surrogate diluted out.

e) Reanalyze the sample or extract if the steps above fail to reveal a problem. If reanalysis of the extracts yields surrogate spike recoveries within the stated limits, then the reanalysis data will be used. Both the original and reanalysis data will be reported.

15.1.2 Matrix Spikes/Matrix Spike Duplicates

The matrix spike criteria for data validity are as follows:

- The average of the percent recoveries for all compounds must fall between 20 and 150 percent.

- Only one compound can be below its required minimum percent recovery.

If the matrix spike criteria are not met, the matrix spike analysis will be repeated. If the subsequent matrix spike analysis meets the criteria, the data will be considered valid. Both matrix spike and surrogate spike recoveries will be used in assessing quality assurance/quality control for RMAL's analytical work.

15.1.3 Blanks

If non-carcinogenic PAH are detected in any Low-Level QC method blanks above the MDL but less than 5 times the MDL the corrective action will consist of flagging the data and investigating the source of the problem to implement a corrective action for future work. If the concentration of carcinogenic PAH in the method blank exceeds the MDL or the concentration of non-carcinogenic PAH in the method blank exceeds five times the MDL, additional corrective action, including but not limited to, reanalyses of the blank and reanalyses of the samples may be required.

If target compounds are detected in Non-Criteria method blanks above 10 micrograms per liter, the corrective action will consist of flagging the data and investigating the source of the problem to implement a corrective action for future work.

The relative concentration of compounds in both the samples and the blank are assessed as part of this corrective action. The results of these activities are documented in the narrative.

15.2 Other Corrective Actions

These sections discuss corrective actions which will be taken in the event that a sample or sample extract is lost or destroyed during shipment, storage or analysis, or in performance and system audits.

15.2.1 Samples

In order to minimize the possibility of sample destruction during shipment, six 1-liter bottles will be taken for all Low-Level (ppt) samples. For all samples, field blanks and matrix spikes and duplicates, subsequent extraction and analysis will be conducted on four intact 1-liter bottles. All field the sample set and the duplicate will be extracted and held. In the event that the field blank is lost during analysis or invalidated, the duplicate field blank will be analyzed and reported. Additional sample matrix will be required for matrix spike analyses.

If less than four liters of a sample remains after shipment and storage for analysis, the Program Manager will be notified and another sample will be collected and shipped to the laboratory for analysis. The analysis report for the sample batch containing the affected sample will clearly note in the discussion section that a replacement sample was taken.

15.2.2 Sample Extracts

If a sample extract is broken or lost during analysis, the Program Manager will be notified and will be responsible for determining the need for replacing the lost sample. The analysis report for the sample batch containing the affected sample will clearly note in the discussion section the action taken.

15.2.3 Quality Control Samples

If a method blank, or matrix spike and its duplicate is lost or broken during analysis, a replacement QC sample will be sampled and analyzed. The analysis report will clearly note that a replacement QC sample was analyzed.

If a field blank is lost or broken during shipment, storage, or analysis, its duplicate will be analyzed. The analysis report for the sample batch associated with the field blank will clearly note the occurrence in the discussion section.

15.2.4 Performance and System Audits

Each system audit is immediately followed by a debriefing, in which the auditor discusses his findings with the laboratory representatives. The debriefing serves a two-fold purpose. First, laboratory management is afforded an early summary of findings, which allows them to begin formulating corrective strategies, and second, the auditor has a chance to test preliminary conclusions and to correct any misconceptions before drafting his report.

The systems audit report (which may or may not contain performance audit findings) is first issued in draft to the Laboratory Quality Control Director. The QC Director distributes the draft to the Laboratory Director and appropriate supervisors to solicit comments and/or rebuttals. These responses are forwarded, in writing, to the auditor. The auditor makes revisions to the draft, on the basis of these responses, at his discretion. Any points of disagreement between the QA department and the laboratory organization are resolved through discussion before the final report is issued. Written responses to the draft report are attached to the final report as an appendix.

Final audit reports are issued to project management and to corporate management. Items requiring corrective action are documented on a Corrective Action Request Form addressed to the Project Manager. One copy is retained by QA upon issuance. The Project Manager receives the original and one copy. When satisfactory progress has been achieved on each requested action, the Project Manager or designee enters descriptions of actions and results on the form, then retains the copy and returns the original to QA to close the loop.

16. QUALITY ASSURANCE REPORTS TO MANAGEMENT

Executing and administering an effective QA program in a large and complex laboratory system demands the skills of a highly qualified staff. The organizational structure of Enseco's Quality Assurance Group (Fig. 16-1) provides a disciplined national management network which oversees and regulates all laboratory QA functions.

Enseco's Quality Assurance Group is headed by Kathleen A. Carlberg, Corporate Vice President of Quality Assurance, who reports directly to the Enseco Executive Committee and to the Chairman of the Board. As principal architect of Enseco's QA program, Ms. Carlberg has charted a rigid course to monitor and control laboratory operations. This involves the intricate process of developing QA manuals, QC protocols, training programs, Standard Operating Procedures (SOP's), uniform statistical data, interlaboratory and intralaboratory performance evaluation studies, and internal auditing programs. Ms. Carlberg is responsible for the administration and implementation of the QA program at all Enseco laboratories.

Laboratory QA activities are specifically designed to fulfill the requirements of both the individual laboratory and Enseco. Directing these activities as Division Director, Mark J. Bollinger, Ph.D. works closely with the laboratory Quality Assurance Director, Gary Torf, who enforces and monitors the program.

Because a QA program undergoes its most stringent test at the laboratory level, Laboratory QA Officers hold a cornerstone position in the organizational structure. Enseco QA Officers are highly skilled analytical scientists, knowledgeable in all aspects of laboratory operations. Their responsibilities include diagnosing quality defects and resolving problems with the analytical system; conducting performance evaluation studies, in-house audits, and walk-throughs; performing statistical analyses of data; auditing spike sample results; enforcing chain-of-custody procedures; assisting in the development of QA manual, SOPs and QC protocols; conducting QA training programs; and maintaining extensive records and archives of all QA/QC data.

Laboratory QA Officers report to both the laboratory president and to Ms. Carlberg. They also interface with one another in a peer evaluation and auditing system that encourages assistance and feedback, problem analysis, and collaboration on ways to improve laboratory performance.

In conjunction with the Laboratory QA Department, laboratory vice presidents, directors, and managers are responsible for a subset of QA activities, and work closely with supervisors to evaluate daily laboratory functions.

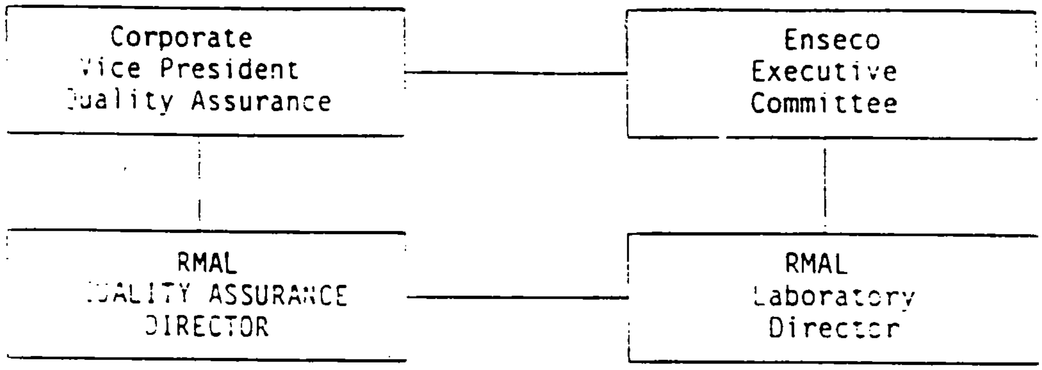

FIGURE 16-1 ENSECO QUALITY ASSURANCE GROUP ORGANIZATION CHART

The reporting system is a valuable tool for measuring the overall effectiveness of the QA program. It serves as an instrument for evaluating the program design, identifying problems and trends, and planning for future needs. Divisional QA Directors submit extensive monthly reports to the VP of QA and the Divisional Director. These reports include:

- The results of the monthly systems audit including any corrective actions taken;
- Performance evaluation scores and commentaries;
- Results of site visits and audits by regulatory agencies and clients;
- Performance on major contracts, (including CLP);
- Problems encountered and corrective actions taken;
- Holding time violations; and
- Comments and recommendations.

In addition, on a weekly basis, a summary of the 5% QA audit of reported data is sent to the Corporate QA Office.

The VP of QA submits weekly reports to the CEO and monthly report to the Enseco Management Committee and each Divisional Director. These reports summarize the information gathered through the laboratory reporting system and contain a thorough review and evaluation of laboratory operations throughout Enseco.

APPENDIX A

STANDARD OPERATING PROCEDURES

INDEX OF STANDARD OPERATING PROCEDURES

Title: Ground-Water Sample Collection from Monitoring Wells
(REFER TO QAPP SECTION 6.5.4.)

1.0 Applicability

This Standard Operating Procedure (SOP) is concerned with the collection of valid and representative samples from ground-water monitoring wells. The scope of this document is limited to field operations and protocols applicable during ground-water sample collection.

2.0 Responsibilities

The site coordinator or his delegate will have the responsibility to oversee and ensure that all ground-water sampling is performed in accordance with the project-specific sampling program and this SOP. In addition, the site coordinator must ensure that all field workers are fully apprised of this SOP. The field team is responsible for proper sample handling as specified in SOP 7510, Handling and Storage of Samples.

3.0 Supporting Materials

The list below identifies the types of equipment which may be used for a range of ground water-sampling applications. From this list, a project-specific equipment list will be selected based upon project objectives, the depth to ground-water, purge volumes, analytical parameters and well construction. The types of sampling equipment are as follows:

- Purging/Sample Collection

  Bailers
  Centrifugal Pump
  Submersible Pump
  Peristaltic Pump

- Sample Preparation/Field Measurement

  pH Meter
  Specific Conductance Meter
  Filtration Apparatus
  Water-Level Measurement Equipment

Additional equipment to support sample collection and provide baseline worker safety will be required to some extent for each sampling task. The additional materials are separated into two primary groups: general equipment which is reusable for several samplings, and materials which are expendable.

- General

  Project-specific sampling program
  Deionized-water dispenser bottle
  Methanol-dispenser bottle
  Site-specific Health & Safety equipment (gloves, respirators, goggles)
  Field data sheets and/or log book
  Preservation solutions
  Sample containers
  Buckets and intermediate containers
  Coolers
  First-Aid kit

- Expendable Materials

  Bailer Cord
  Respirator Cartridges
  Gloves
  Water Filters
  Chemical-free paper towels
  Plastic sheets

Equipment checklists have been developed to aid in field trip organization and should be used in preparation for each trip.

4.0 Water-Level Measurement

4.1 Introduction

Prior to obtaining a water-level measurement, cut a slit in one side of the plastic sheet and slip it over and around the well, creating a clean surface onto which the sampling equipment can be positioned. This clean working area should be a minimum of eight feet square. Care will be taken not to kick, transfer, drop, or in any way let soil or other materials fall onto this sheet unless it comes from inside the well. Do not place meters, tools, equipment, etc. on the sheet unless they have been cleaned first with a clean rag.

After unlocking and/or opening a monitoring well, the first task will be to obtain a water-level measurement. Water-level measurements will be made using an electronic or mechanical device. Electronic measurement devices will be used in all wells wherein a clearly audible sound cannot be produced with a mechanical device.

4.2 Well Security

Unlock and/or open the monitoring well. Enter a description of condition of the security system and protective casing on the Ground-Water Sample Collection Record shown in Figure 1.

4.3 Measuring Point

Check for the measuring point for the well. The measuring point location should be clearly marked on the outermost casing or identified in previous sample collection records. If no measuring point can be determined, a measuring point should be established. Typically the top (highest point) of the protective or outermost well casing will be used as the measuring point. The measuring point location should be described on the Ground-Water Sample Collection Record and should be the same point used for all subsequent sampling efforts.

4.4. Measurement

To obtain a water-level measurement lower a clean steel, fiberglass tape into the monitoring well. Care must be taken to assure that the water-level measurement device hangs freely in the monitoring well and is not adhering to the wall of the well casing. The water-level measuring tape will be lowered into the well until the audible sound of the unit is detected or the light on an electronic sounder illuminates. At this time the precise measurement should be determined (to hundredth of a foot) by repeatedly raising and lowering the tape to converge on the exact measurement. The water-level measurement should be entered on the Ground-Water Sample Collection Record. As well point of measurement should be indicated; i.e., top of protective casing, top of pueriser, ground level.

4.5 Decontamination

The measurement device shall be decontaminated immediately after use with a methanol soaked towel. Generally only that portion of the tape which enters the water table should be cleaned. It is important that the measuring tape is never placed directly on the ground surface.

5.0 Purge-Volume Computation

All monitoring wells to be purged prior to sample collection. Depending upon the ease of purging, 3 to 10 volumes of ground water to be determined by hydrogeologing prior to sampling present in a well

shall be withdrawn prior to sample collection or one volume if well can be purged dry. The volume of water present in each well shall be computed based on the length of water column and well casing diameter. The water volume shall be computed using Figure 2.

6.0 Well-Purging Methods

6.1 Introduction

Purging must be performed for all ground-water monitoring wells prior to sample collection in order to remove stagnant water from within the well casing and ensure that a representative sample is obtained. The following sections explain the proper procedures for purging and collecting water samples from monitoring wells.

Three general types of equipment are used for well purging: bailers, surface pumps, or down-well submersible pumps.

In all cases pH and/or specific conductance will be monitored during purging. Field parameter values will be entered on the Ground-Water Sample Collection Record along with the corresponding purge volume.

6.2 Bailing

In many cases bailing is the most convenient method for well purging. Bailers are constructed using a variety of materials; generally, PVC stainless steel, and Teflon®. Care must be taken to select a specific type of bailer that suits a study's particular needs. Teflon® bailers are generally most "inert" and are used most frequently. Keep in mind the diameter of each monitoring well so that the correct size bailers are taken to the site. It is preferable to use one bailer per well; however, field decontamination is a relatively simple task if required.

Bailing presents two potential problems with well purging. First, increased suspended solids may be present in samples as a result of the turbulence caused by raising and lowering the bailer through the water column. High solids concentrations may require that total suspended solids (TDS) and the chemical character of solids be evaluated during sample analyses. Second, bailing may not be feasible for wells which require that greater than twenty (20) gallons be removed during purging. Such bailing conditions mandate that long periods be spent during purging and sample collection or that centrifugal pumps be used. All ground-water collected from monitoring wells for subsequent volatile organic compound analyses shall be collected using bailers, regardless of the purge method.

6.3 Surface Pumping

Ground-water withdrawal using pumps located at the ground surface is commonly performed with centrifugal or peristaltic pumps.

All applications of surface pumping will be governed by the depth to the ground-water surface. Peristaltic and centrifugal pumps are limited to conditions where ground water need only be raised through approximately 20 feet of vertical distance. The lift potential of a surface pumping system will depend upon the net positive suction head of the pump and the friction losses associated with the particular suction line, as well as the relative percentage of suspended particulates.

Surface pumping can be used for many applications of well purging and ground-water sample collection. In all cases, pumping cannot be used for the collection of samples to be analyzed for volatile organic compounds (VOCs).

6.3.1 Peristaltic Pump

Peristaltic pumps provide a low rate of flow typically in the range of 0.02-0.2 gallons/min (75-750 ml/min). For this reason, peristaltic pumps are not particularly effective for well purging. Peristaltic pumps are suitable for purging situations where disturbance of the water column must be kept minimal for particularly sensitive analyses. Peristaltic pumps are most often used in conjunction with field filtering of samples and therefore can be used to obtain water samples for direct filtration at the wellhead.

6.3.2 Centrifugal Pump

Centrifugal pumps are designed to provide a high rate of pumping, in the range of 10-40 gallons per minute (gpm), depending on pump capacity. Discharge rates can also be regulated somewhat provided the pump has an adjustable throttle.

When centrifugal pumps are used, samples should be obtained from the suction (influent) line during pumping by an entrapment scheme as shown in Figure 3. Construction of this sampling scheme is relatively simple and will not be explained as part of this SOP. It is suggested that if samples cannot be obtained before going through the pump, that samples be obtained by using a bailer once pumping has ceased. Collecting samples from the pump discharge is not recommended.

6.3.3 Submersible Pump

Submersible pumps provide an effective means for well purging and in some cases sample collection. Submersible pumps are particularly useful for situations where the depth to water table is greater than twenty (20-30) feet and the depth or diameter of the well requires that a large purge volume be removed during purging.

ERT uses the Johnson-Keck pump model SP-81 which has a 1.75 inch diameter pump unit. The pump diameter restricts use to monitoring wells which have inside diameters equal to or greater than two (2) inches. As with other pump-type purge/sample collection methods, submersible pumps will not be used for the collection of samples for analyses of volatile organic compounds. Submersible pumps should never be used for well development as this <u>will</u> seriously damage the pump.

7.0 Sample Collection Procedures

7.1 Bailing

Obtain a clean/decontaminated bailer and a spool of polypropylene rope or equivalent bailer cord. Using the rope at the end of the spool tie a bowline knot or equivalent through the bailer loop. Test the knot for security and the bailer itself to ensure that all parts are intact prior to inserting the bailer into the well.

Remove the protective foil wrapping from the bailer, and lower the bailer to the bottom of the monitoring well and cut the cord at a proper length. Boiler rope should never touch the ground surface at any time during the purge routine.

Raise the bailer by grasping a section of cord using each hand alternately in a "rocking" action. This method requires that the samplers' hands be kept approximately 2-3 feet apart and that the bailer rope is alternately looped onto or off each hand as the bailer is raised and lowered.

Bailed ground water is poured from the bailer into a graduated bucket to measure the purged water volume.

For slowly recharging wells, the bailer is generally lowered to the bottom of the monitoring well and withdrawn slowly through the entire water column. Rapidly recharging wells should be purged by varying the level of bailer insertion to ensure that all stagnant water is removed. The water column should be allowed to recover to 70-90% of its static volume prior to collecting a sample. Water samples should be obtained from midpoint or lower within the water column.

Samples collected by bailing will be poured directly into sample containers from bailers which are full of fresh ground water. During sample collection, bailers will not be allowed to contact the sample containers.

7.2 Peristaltic Pump

Place a new suction and discharge line to the peristaltic pump. Silicon tubing must be used through the pump head. A second type of tubing may be attached to the silicon tubing to create the suction and discharge lines. Such connection is advantageous for the purpose of reducing tubing costs, but can only be done if airtight connections can be made. Tygon tubing will not be used when performing well purging or collecting samples for organic analysis. The suction line must be long enough to extend to the static ground-water surface and reach further should drawdown occur during pumping.

Measure the length of the suction line and lower it down the monitoring well until the end is in the upper 2-5 inches of the water column present in the well. Start the pump and direct the discharge into a graduated bucket.

Measure the pumping rate in gallons per minute by recording the time required to fill a selected volume of a bucket. Flow measurement shall be performed three times to obtain an average rate.

The pumping shall be monitored to assure continuous discharge. If drawdown causes the discharge to stop, the suction line will be lowered very slowly further down into the well until pumping restarts.

Measurements of pH and specific conductance will be made periodically during well purging. All readings will be entered on the Ground-Water Sample Collection Record.

Samples will be collected after the required purge volume has been withdrawn and the field parameters (pH and Specific Conductance) have stabilized.

When the sample bottles are prepared, each shall be filled directly from the discharge line of the peristaltic pump. Care will be taken to keep the pump discharge line from contacting the sample bottles. Ground-water samples requiring filtration prior to placement in sample containers, will be placed in intermediate containers for subsequent filtration or filtered directly using the peristatic pump.

At each monitoring point when use of the peristaltic pump is complete, all tubing including the suction line, pump head and discharge line must be disposed of. In some cases where sampling will be performed frequently at the same point, the peristaltic pump tubing may be retained between each use in a clean zip-lock plastic bag.

7.3 Centrifugal Pump

7.3.1 Direct Connection Method (Note: This method requires that the well casing be threaded at the top.)

Establish direct connection to the top of the monitoring well if possible using pipe connections, extensions, and elbows, with Teflon® tape wrapping on all threaded connections. If the centrifugal pump will subsequently be used for sample collection, a sample isolation chamber will be placed in the suction line configuration as shown in Figure 3.

Prime the pump by adding tap water to the pump housing until the housing begins to overflow.

Start the pump and direct the discharge into a graduated bucket or a bucket of known capacity (>2.5 gallons).

Start the pump and measure the pumping rate in gallons per minute by recording the time required to fill the graduated bucket. Flow measurement should be checked periodically to determine if pumping rates are continuous, fluctuating, or diminishing. If discharge stops, the pump will be throttled back to determine if pumping will restart at a lower rate. If pumping does not restart, the pump should be shut off to allow the well to recharge.

Measurements of pH and specific conductance will be made periodically during well purging. All readings will be entered on the Ground-Water Sample Collection Record. Samples will be collected after the required purge volume has been withdrawn and the field parameters (pH and Specific Conductance) have stabilized. Samples should be collected from an in-line discharge valve or with a bailer. The pump should be properly decontaminated between wells.

7.3.2 Down-Well Suction-Line Method

Lower a new suction line into the well. The suction line will have a total length great enough to extend to the water table and account for a minimum of five (5) feet of drawdown. Note should be made that drawdown may exceed the depth where pumping will terminate as a result of a limitation derived from suction-line conditions and the lift potential of the pump. All connections should be made using Teflon® ferrules and Teflon® thread wrapping tape. Run the pump as per Section 7.3.1.

At each monitoring well when use of a centrifugal pump is complete, all suction line tubing should be disposed of properly.

7.4 Submersible Pump

Prior to using a submersible pump, a check will be made of well diameter and alignment. A 1.75 inch diameter decontaminated cylindrical tube should be lowered to the bottom of each monitoring well to determine if the alignment or plumbness of a well is adequate to accommodate the submersible pump. All observations will be entered in the Ground-Water Sample Collection Record.

Slowly lower the submersible pump into the monitoring well taking notice of any roughness or restrictions within the riser.

Count the graduations on the pump discharge line and stop lowering when the stainless steel portion is below the uppermost section of the static water column within monitoring well. Secure the discharge line and power cord to the well casing.

Connect the power cord to the power source (i.e., rechargeable battery pack or auto battery monitor) and turn the pump on (forward mode). When running, the pump can usually be heard by listening near the well head.

Voltage and amperage meter readings on the pump discharge must be checked continuously. The voltage reading will decline slowly during the course of a field day representing the use of power from the battery. Amperage readings will vary depending upon the depth to water table. Amperage readings greater than 10 amps usually indicate a high solids content in the ground water which may cause pump clogging and serious damage. If a steady increase in amperage is observed, the pump should be shut off, allowed to stop, switched to the reverse mode, stopped again and then placed in forward mode. If high amperage readings persist, the pump should be withdrawn and checked using the large upright cylinder and tap water. Ground-water conditions such as high solids may require that an alternate purge/sample method be used.

Drawdown must also be monitored continuously by remaining near the well at all times and listening to the pump. When drawdown occurs, a metallic rotary sound will be heard as the pump intake becomes exposed and ceases to discharge water, but continues to run. The pump should be lowered immediately to continue pumping water within the uppermost section of the static water column. NOTE: The submersible pump cannot be allowed to run while not pumping for more than five seconds or the pump motor will burn out.

If drawdown continues to the extent that the well is pumped dry, the pump should be shut off and the well allowed to recharge. This on/off cycle may need to be repeated several times in order to purge the well properly.

Measurements of the pumping rate, pH, and specific conductance should be made periodically during well purging. All readings and respective purge volumes should be entered on the Ground-Water Sample Collection Record.

While pumping is on-going and when sample bottles are prepared, bottles will be filled directly from the discharge line of the pump taking care not to touch sample bottles to the discharge line.

At each monitoring well when use of the submersible pump is complete, the pump, discharge line and power cord shall be decontaminated according to the procedures contained in the SOP for Decontamination.

8.0 Sample Preparation

8.1 Introduction

Prior to sample transport or shipment, ground-water samples may require filtration and/or preservation dependent on the specific type of analysis required.

Specific preservation techniques are described in the EPA document, Handbook for Sampling and Sample Preservation of Water and Wastewater (EPA-600/4-82-029). The EPA manual and laboratory manager should be consulted during the planning stage of the project. Project-specific sampling plans shall be assembled using the approved procedures obtained from the EPA manual.

8.2 Filtration

Ground-water samples collected for dissolved metals analyses will be filtered prior to being placed in sample containers. Ground-water filtration will be performed using a peristaltic pump and a 0.45 micron, water filter. Typically the water filters are 142 mm in diameter and are usually placed in 142 mm polycarbonate housings.

The filtration of ground-water samples shall be performed either directly from the monitoring well or from intermediate sample containers such as decontaminated buckets. In either case, well purging shall be performed first. Fresh ground water shall then be filtered and discharged from the filtration apparatus directly into sample containers. For most dissolved metal analyses, pH adjustment of the sample is also required and shall be performed after filling the sample bottles. This is generally accomplished using laboratory supplied compounds such as sulfuric or nitric acid and sodium hydroxide.

9.0 Documentation

A number of different documents must be completed and maintained as a part of ground-water sampling effort. The documents provide a summary of the sample-collection procedures and conditions, shipment method, the analyses requested and the custody history. The list of documents is:

- Ground-water sample collection record
- Sample labels
- Chain of custody forms and tape
- Shipping receipts

Sample labels shall be completed at the time each sample is collected and will include the information listed below. A sample label is shown in Figure 4.

- Client or project name
- Sample number
- Designation (i.e., identification of sample point no.)
- Analysis
- Preservative (e.g., filtration, acidified pH<2 HNO_3)
- Sample-collection date
- Sampler's name

Figure 5 displays the chain of custody record used by ERT. The chain of custody form is the record sample collection and transfer of custody. Information such as the sample collection date and time of collection, sample identification and origination, client or project name shall be entered on each chain of custody record. In accordance with 40 CFR 261.4(d) the following information must accompany all ground water samples which are known to be non-hazardous and to which U.S. Department of Transportation and U.S. Post Office regulations do not apply. Such information is:

- sample collector's name, mailing address and telephone number,
- analytical laboratory's name, mailing address and telephone number,
- quantity of each sample,
- date of shipment, and
- description of sample.

The chain of custody forms provide a location for entry of the above-listed information.

10.0 References

EPA, Handbook for Sampling and Sample Preservation of Water and Wastewater EPA-600/4-82-029, September 1982.

Geotrans, Inc. RCRA Permit Writer's Manual, Ground-Water Protection prepared for U.S. EPA. Contract No. 68-01-6464, October 1983.

Code of Federal Regulations, Chapter 40 (Section 261.4(d).

Figure 1

ENSR

Well No ______

GROUND WATER SAMPLE COLLECTION RECORD

Job No ______ Date ______

Location ______ Time S ______

Weather Conds ______ E ______

1. WATER LEVEL DATA (from ToC) ToC Elevation (from LS) ______

a Total Well Length (- TC) ______ known, meas. Tape Corr (TC) ______

b Water Table Elev (+ TC) ______ Well Dia ______

c Length of Water Column ______ (a-b)

2. WELL PURGING DATA

a Purge Method ______

b Required Purge Volume (@ ____ well volumes) ______

c Field Testing: Equipment Used ______

Volume Removed	T°	PH	Spec Cond.	Color

3 Sample Collection Method ______

Container Type	Preservation	Analysis Req

Comments ______

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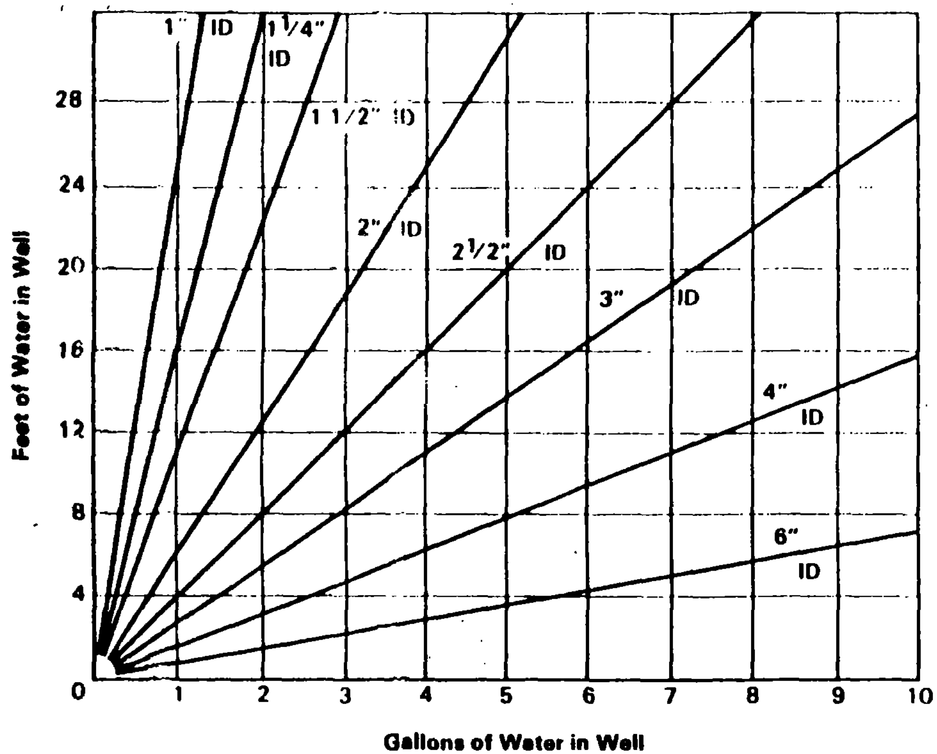

(a) Graphical Explanation

Volume/Linear Ft. of Pipe		
ID(in)	Gal	Liter
1/4	0.003	0.010
3/8	0.006	0.022
1/2	0.010	0.039
3/4	0.023	0.087
1	0.041	0.154
2	0.163	0.618
3	0.367	1.39
4	0.653	2.47
6	1.47	5.56

(b) Volume Factors

Figure 2 Purge Volume Computation

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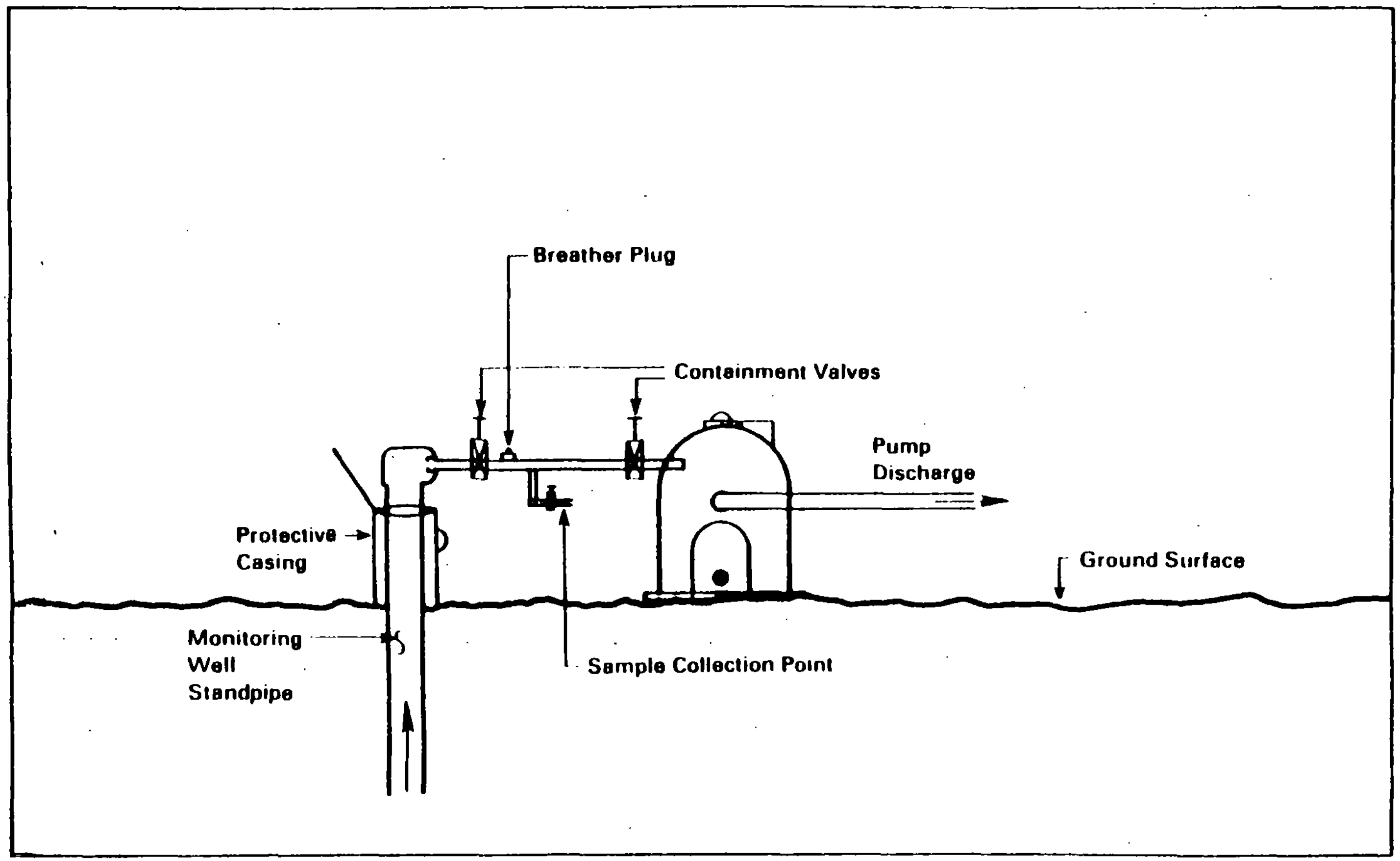

Figure 3 Down Well Suction Line Configuration

CLIENT ____________________

SAMPLE NO. ____________________

DESIGNATION ____________________

ANALYSIS ____________________

PRESERVATIVE ____________________

DATE __________ BY __________

Figure 4 Sample Container Label

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CHAIN OF CUSTODY RECORD

Client/Project Name	Project Location	ANALYSES
Project No.	Field Logbook No.	
Sampler: (*Signature*)	Chain of Custody Tape No.	

Sample No./ Identification	Date	Time	Lab Sample Number	Type of Sample							REMARKS

Relinquished by: (*Signature*)	Date	Time	Received by: (*Signature*)	Date	Time
Relinquished by: (*Signature*)	Date	Time	Received by: (*Signature*)	Date	Time
Relinquished by: (*Signature*)	Date	Time	Received for Laboratory: (*Signature*)	Date	Time
Sample Disposal Method	Disposed of by: (*Signature*)			Date	Time
SAMPLE COLLECTOR	ANALYTICAL LABORATORY			No.	

1974 3 84

Figure 5 Sample Chain of Custody Record

1.0 Applicability

This Standard Operating Procedure (SOP) is concerned with procedures associated with the packaging and shipment of samples. Two general categories of samples exist: environmental samples consisting of air, water and soil; and waste samples which include non-hazardous solid wastes and hazardous wastes as defined by 40 CFR Part 261.

2.0 Responsibilities

It is the responsibility of the project manager to assure that the proper packaging and shipping techniques are utilized for each project. The site operations manager shall be responsible for the enactment and completion of the packaging and shipping requirements outlined in the project specific sampling plan. The site operations manager shall be responsible to research, identify and follow all applicable U.S. Department of Transportation (DOT) regulations regarding shipment of materials classified as waste.

3.0 General Method

The objective of sample packaging and shipping protocol is to identify standard procedures which will minimize the potential for sample spillage or leakage and maintain field sampling program compliance with U.S. EPA and U.S. DOT regulations.

The extent and nature of sample containerization will be governed by the type of sample, and the most reasonable projection of the sample's hazardous nature and constituents. The EPA regulations (40 CFR Section 261.4(d)) specify that samples of solid waste, water, soil or air, collected for the sole purpose of testing, are exempt from regulation under the Resource Conservation and Recovery Act (RCRA) when all of the following conditions are applicable:

A. Samples are being transported to a laboratory for analysis;
B. Samples are being transported to the collector from the laboratory after analysis;
C. Samples are being stored (1) by the collector prior to shipment for analyses, (2) by the analytical laboratory prior to analyses, (3) by the analytical laboratory after testing but prior to return of sample to the collector or pending the conclusion of a court case.

Qualification for categories A and B above require that sample collectors comply with U.S. DOT and U.S. Postal Service (USPS) regulations or comply with the following items if U.S. DOT and USPS regulations are found not to apply:

The following information must accompany all samples and will be entered on a sample specific basis on chain of custody records:

- sample collector's name, mailing address and telephone number,
- analytical laboratory's name, mailing address and telephone number,
- quantity of sample,
- date of shipment,
- description of sample, and

in addition, all samples must be packaged so that they do not leak, spill or vaporize.

4.0 General Methods

4.1 Place plastic bubble wrap matting over the base and bottom corners of each cooler or shipping container as needed to manifest each sample.

4.2 Obtain a chain of custody record as shown in Figure 1 and enter all the appropriate information as discussed in Section 3.0 of this SOP. Chain of custody records will include complete information for each sample. One or more chain of custody records shall be completed for each cooler or shipping container as needed to manifest each sample.

4.3 Wrap each sample bottle individually and place standing upright on the base of the appropriate cooler, taking care to leave room for some packing material and ice or equivalent. Rubber bands or tape should be used to secure wrapping, completely around each sample bottle.

4.4 Place additional bubble wrap and/or styrofoam pellet packing material throughout the voids between sample containers within each cooler.

4.5 Place ice or cold packs in heavy duty zip-lock type plastic bags, close the bags, and distribute such packages over the top of the samples.

4.6 Add additional bubble wrap/styrofoam pellets or other packing materials to fill the balance of the cooler or container.

4.7 Obtain two pieces of chain of custody tape as shown in Figure 2 and enter the custody tape numbers in the appropriate place on the chain of custody form. Sign and date the chain of custody tape.

4.8 To complete the chain of custody form enter the type of analysis required for each sample, by container, under the "ANALYSES" section. Under the specific analysis enter the quantity/volume of sample collected for each corresponding analysis.

If shipping the samples where travel by air or other public transportation is to be undertaken, sign the chain of custody record thereby relinquishing custody of the samples. Relinquishing custody should only be performed when directly transmitting custody to a receiving party or when transmitting to a shipper for subsequent receipt by the analytical laboratory. Shippers should not be asked to sign chain of custody records.

4.9 Remove the last copy from the chain of custody record and retain with other field notes. Place the original and remaining copies in a zip-lock type plastic bag and place the bag on the top of the contents within the cooler or shipping container.

4.10 Close the top or lid of the cooler or shipping container and with another person rotate/shake the container to verify that the contents are packed so that they do not move. Improve the packaging if needed and reclose.

When transporting samples by automobile to the laboratory, and where periodic changes of ice are required, the cooler should only be temporarily closed so that reopening is simple. In these cases, chain of custody will be maintained by the person transporting the sample and chain of custody tape need not be used. If the cooler is to be left unattended, then chain of custody procedures should be enacted.

4.11 Place the chain of custody tape at two different locations on the cooler or container lid and overlap with transparent packaging tape. For coolers with hinged covers, if the hinges are attached with screws, chain of custody tape should also be used on the hinge side.

4.12 Packaging tape should be placed entirely around the sample shipment containers. A minimum of one to two full wraps of packaging tape will be placed at at least two places on the cooler. Shake the cooler again to verify that the sample containers are well packed.

4.13 If shipment is required, transport the cooler to an overnight express package terminal or arrange for pickup. Obtain copies of all shipment records as provided by the shipper.

4.14 If the samples are to travel as luggage, check with regular baggage.

4.15 Upon receipt of the samples, the analytical laboratory will open the cooler or shipping container and will sign "received by laboratory" on each chain of custody form. The laboratory will verify that the chain of custody tape has not been broken previously and that the chain of custody tape number corresponds with the number on the chain of custody record. The analytical laboratory will then forward the back copy of the chain of custody record to the sample collector to indicate that sample transmittal is complete.

5.0 Documentation

As discussed in Section 4.0 the documentation for supporting the sample packaging and shipping will consist of chain of custody records and shipper's records. In addition a description of sample packaging procedures will be written in the field log book. All documentation will be retained in the project files following project completion.

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CHAIN OF CUSTODY RECORD

Client/Project Name	Project Location	ANALYSES
Project No.	Field Logbook No.	
Sampler: (*Signature*)	Chain of Custody Tape No.	

Sample No./ Identification	Date	Time	Lab Sample Number	Type of Sample							REMARKS

Relinquished by: (*Signature*)	Date	Time	Received by: (*Signature*)	Date	Time
Relinquished by: (*Signature*)	Date	Time	Received by: (*Signature*)	Date	Time
Relinquished by: (*Signature*)	Date	Time	Received for Laboratory: (*Signature*)	Date	Time
Sample Disposal Method:	Disposed of by: (*Signature*)			Date	Time

SAMPLE COLLECTOR ERT - A Resource Engineering Company 696 Virginia Road Concord, MA 01742 617 369 8910	ANALYTICAL LABORATORY	ENSR Nº 1663

1974 3 84

Figure 1

PROCEDURES FOR GROUND WATER MONITORING:

Minnesota Pollution Control Agency Guidelines

April 1985

By

Gretchen V. Sabel
Pollution Control Specialist

Thomas P. Clark
Senior Hydrologist

This procedures manual was developed in July 1983 as one of the elements of the Minnesota Pollution Control Agency Ground Water Protection Strategy Work Plan, and revised following a lengthy comment and field trial period.

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Minnesota Pollution Control Agency
Solid and Hazardous Waste Division
Program Development Section
612/296-7739

(REFER TO QAPP SECTION 6.5.4.)

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Special thanks go to the Program Development Section clerical staff for their typing of the many drafts and revisions of this document, and to Len Nelson, who drafted most of the diagrams and provided us with the cover art.

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control. Laboratory precision and accuracy data should be submitted to the Agency as a part of the quality assurance plan described in Section 9.

Error can be introduced at each stage of monitoring, including installation of monitoring devices, sampling from monitoring points, and analysis. It is the responsibility of all who are involved to keep this error to a minimum. Providing accurate and meaningful data the first time is to everyone's benefit.

Monitoring is not an end in itself. Rather it should be thought of as a tool used to measure a site design's efficiency at controlling water pollution. Continued monitoring is required after corrective measures have been taken to verify that water quality improves over time.

SECTION 2

MONITORING WELLS

Monitoring Well Construction

Construction of all water wells, including monitoring wells, is under the jurisdiction of the Minnesota Department of Health (MDH). The wells must be installed by either a licensed well driller or an engineer registered with the MDH to install monitoring wells. All applicable construction standards included in the Minnesota Water Well Construction Code must be met. The current standards are found in 7 MCAR §§ 1.210-1.224,* copies of which are available for a fee by writing:

Minnesota Department of
 Administration
Documents Section
117 University Avenue
St. Paul, Minnesota 55155

The construction code is currently being amended to include separate specific requirements for ground water monitoring well construction. Figure 1 shows a well which meets current (March 1985) construction requirements.

Details of monitoring well construction will be determined by site-specific factors such as required depth of monitoring wells, waste types, and expected aquifer yield. For that reason, a detailed monitoring system plan showing geologic stratigraphy, well locations (both horizontally and vertically) and well construction details must be

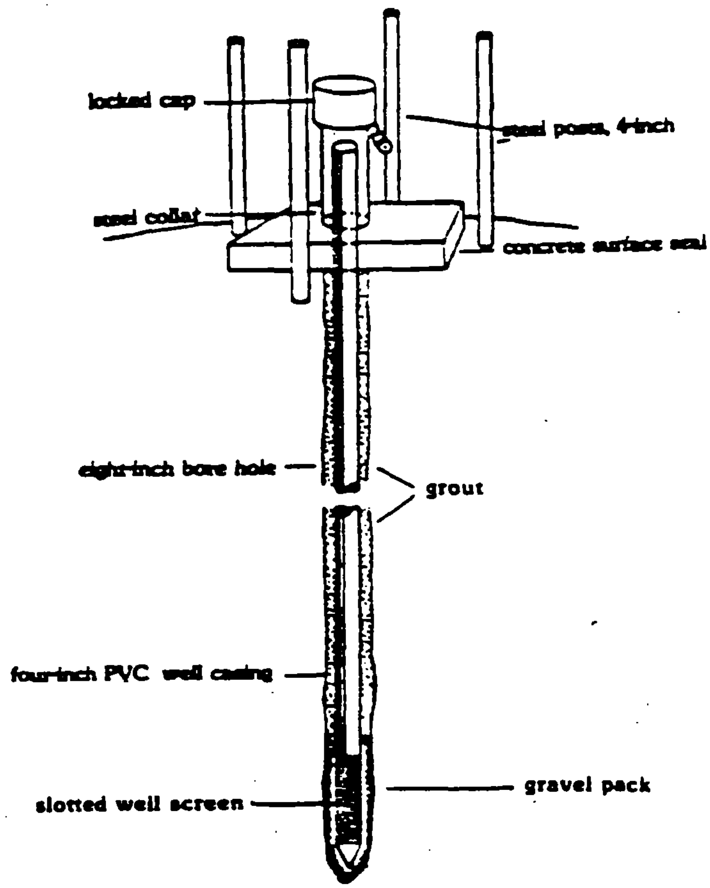


Figure 1. Monitoring Well Construction

*Subject to recodification in 1985, the Minnesota Water Well Construction Code will be found in Minnesota Rules Chapter 4725 (1985).

submitted to the Agency for approval prior to installation. Approval must also be obtained from the MDH before installation of wells which penetrate one or more confining beds. See "Guidelines for Ground Water Monitoring System Design" (MPCA, 1985) for a more detailed discussion of monitoring network design.

Some specific requirements follow.

Well labeling:

Each well should be permanently labeled with its assigned monitoring point identification. The label should be consistent with the identification used in site plans and monitoring reports. One way to permanently label a well would be to inscribe the well identification number and the date of installation in the concrete slab surrounding the well collar while it is still wet. Alternately, the information may be etched or painted directly on the well collar.

Well diameters:

Wells must be constructed to facilitate sampling. Wells which are installed with water levels below the suction limit (approximately 25-30 feet) and which are too narrow in diameter to allow for sampling with a conventional submersible pump are unacceptable. Consideration should be given to the sampling method to be used when planning well construction. For wells less than 25 feet deep, a 2-inch diameter is sufficient because the wells may be sampled with a peristaltic pump. Two-inch wells, 25-125 feet deep, may be sampled with a 2-inch submersible pump, but these units are costly. In some instances, it may be more cost-effective to install 4-inch wells which can be sampled with less expensive, higher capacity submersible pumps. Wells greater than 125 feet deep should be at least 4 inches in diameter to allow for sampling with conventional submersible pumps. The Minnesota Water Well Construction Code requires a 2-inch annulus surrounding the well casing.

Casing material:

Well casings must meet MDH requirements, which currently allow only the use of PVC or ABS plastic, ferrous materials or stainless steel. A general rule of thumb is to choose threaded plastic pipe where metals and physical parameters are to be tested, ferrous pipe where organics alone are to be tested, and stainless steel where all types of parameters are to be tested. Since the casing material can cause interferences with some tests, it may be advisable to install 4-inch wells so that higher capacity pumps can be used to reduce casing influences on the sampled water quality. When PVC casing is installed, schedule 80 should be used to meet MDH strength requirements.

All materials used in well construction should be as clean as possible before installation. Washing with tap water is acceptable for general applications. More rigorous procedures, such as steam cleaning or hexane and distilled water rinses, are necessary when monitoring for very low levels of some contaminants. Care should be taken when using plastic pipe that solvent-welding compounds are not used, and that any cleaning fluids used are rinsed off with distilled water prior to installation. At least one screen and casing manufacturer offers a cleaning service, providing the parts hermetically sealed in plastic bags for transport to the drill site.

Well screens and filter packs:

Well screen slots should be sized as large as possible to allow proper development, while preventing sediment from entering the well. Slot size should be based on grain-size distribution and hydrologic characteristics of the aquifer being monitored. Filter packs of washed sand or gravel are often necessary to produce sediment-free water for testing. Filter pack materials and grout should not be poured in from the surface. The Agency recommends these materials be placed from the bottom of the borehole using tremie pipes. Centering guides should be used on the screen and casing so the filter packs and grout can be placed uniformly around the well.

Grouting:

The annulus around the casing should be sealed with neat cement grout to prevent the flow of contaminated water along the casing. The use of bentonite is discouraged because its composition can vary widely, depending upon its source, which may subsequently affect the water quality analyses from that well. A small amount of bentonite (2%) may be added to the cement, however, to minimize shrinkage.

Well development:

Monitoring wells must be capable of producing nearly sediment-free water to provide meaningful analytical results. Thorough well development is therefore essential. The combined use of a jetting tool with air-lift pumping is a particularly effective development method. Mechanical surging as with a surge block or large bailer can also be used, but is less effective. Over-pumping is not recommended, as it may cause bridging of sand particles in the sand pack or formation.

Recent work suggests that wells in tight formations may be more effectively developed if the standing water is gently removed as it recharges the well, rather than agitating the walls of the annulus with the more aggressive development techniques. This benign development technique may take a longer period of time to successfully accomplish, but once complete can improve the yield of a well which otherwise would only provide marginal yield for sampling.

Well installation in areas of known or suspected contamination:

When working in areas of known or suspected contamination, or in any areas which may be affected by pollution sources, extreme care must be taken to avoid spreading contamination during the drilling operation. Drill stems and all down-hole equipment should be thoroughly steam-cleaned and, in some instances, hexane-rinsed to avoid spreading contaminants to uncontaminated areas of the site. Native soil should not be used as backfill. Clean sand should be brought in instead. Wells which penetrate a confining bed are required by MDH to be constructed with double casings.

Well drilling methods:

Wells may be drilled by a number of methods, a good discussion of which is given in "Manual of Ground-Water Sampling Procedures" (Scalf, 1981). The use of drilling fluids and muds is discouraged because of possible analytical interferences and well screen clogging.

Well drilling and construction logs:

High-quality drilling and laboratory identification logs must be submitted for each well or piezometer. These logs should include at least the following information:

1. Detailed soil or rock description and classification, measured soil and rock properties, sample collection locations and types of collection methods, and elevations of upper and lower contacts. Classification should be done by a qualified geologist or soils specialist. If the methods of drilling and sampling do not permit the soil characteristics and contact elevations to be described accurately and in detail, geophysical logs should be provided.

2. Location referenced to known control points, date of completion, and name, address, and telephone number of person or company responsible for construction of the well.

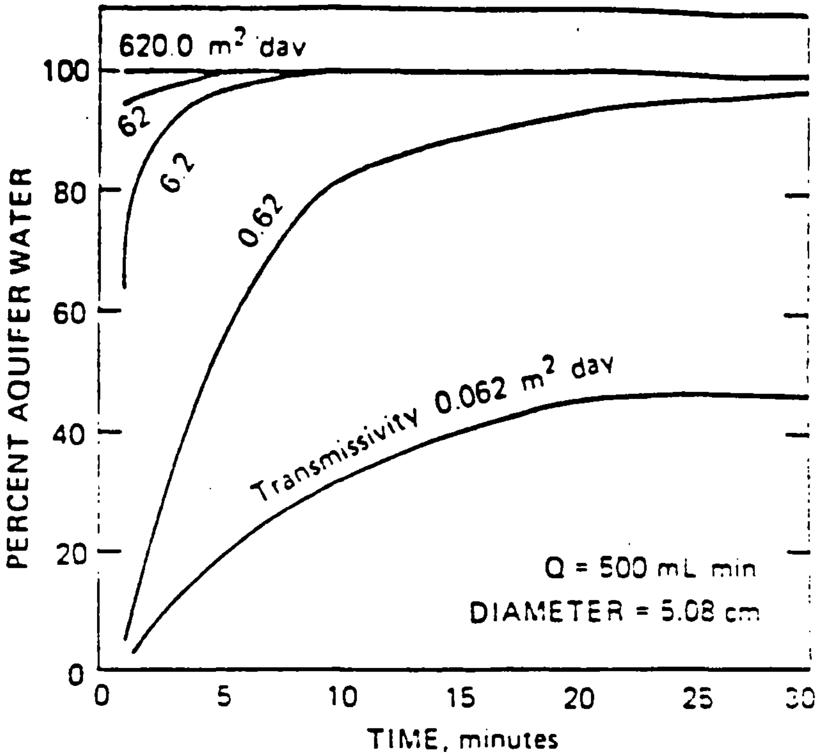
3. Depth of well; construction materials utilized, including well casing type and size, screen opening size; size fraction of screen packing material used for casing and grout; methods used to drill the hole, place the sealed intervals, and develop the well; elevations of the land surface, top of casing, and measured water levels; elevations of the top and bottom of the screen, casing, and each type of backfill or seal; intervals of screen packing material; grouted intervals; and geophysical logs, if any.

Stabilization and Recovery Rate Tests

Once a well is installed and developed, a pumping test of two to three hour duration may be conducted to obtain information on the well's yield potential and relative transmissivity (a measure of the rate at which water can be transmitted) of the aquifer. Recent research by the Illinois State Water Survey (Barcelona, 1983) recommends the short pumping test as a data-gathering method for determining "the frequency at which samples will be collected and the rate and period of time each well should be pumped prior to collecting the sample." Figure 2, from that reference, graphically shows the effect that aquifer transmissivity has on the amount of pumping needed to obtain a sample containing water derived mostly from the aquifer rather than water from storage within the casing and annular space. A more detailed discussion of this concept is given in Gibb, 1981.

While these pumping tests are not currently being required by the Agency on a routine basis, a stabilization test (or, alternately, a recovery rate test) is required for all new wells following development to determine the amount of pumping needed prior to sample collection. To conduct a stabilization test, pump the well to waste at a rate that yields a constant stream of water without dewatering the well. This rate should be equivalent to the rate at which the well will be pumped during sampling. If the well has slow recharge and goes dry with pumping, a recovery rate test should be performed instead. The pump should be set in the upper portion of the water column so that all water standing in the well is drawn out and no stagnant water remains above the pump.

Figure 2. Relationship of Aquifer Transmissivity and Required Well Evacuation (From Barcelona, 1983)



Specific conductance, pH, and temperature should be measured in the field at intervals of one well volume until three successive readings yield equivalent values within the following ranges for each of these parameters:

Specific conductance (temperature-corrected): $\pm$ 10 umhos/cm
pH: $\pm$ 0.1 pH unit
Temperature: $\pm$ 0.5 °C

Once stabilized, samples should be collected without delay. In past versions of this manual, the measurements were to be taken at five minute intervals. Recent Agency experiences with monitoring wells have led to this change in instructions in an effort to avoid over-pumping the sampling wells. A closed, flow-through chamber is helpful for taking the measurements. The device shown in Figure 3 was fabricated by Dale Thompson of the MPCA for sampling at monitoring wells. For additional references on the stabilization test see U.S. Geological Survey, 1976; Gibb, 1981; and MPCA, 1983.

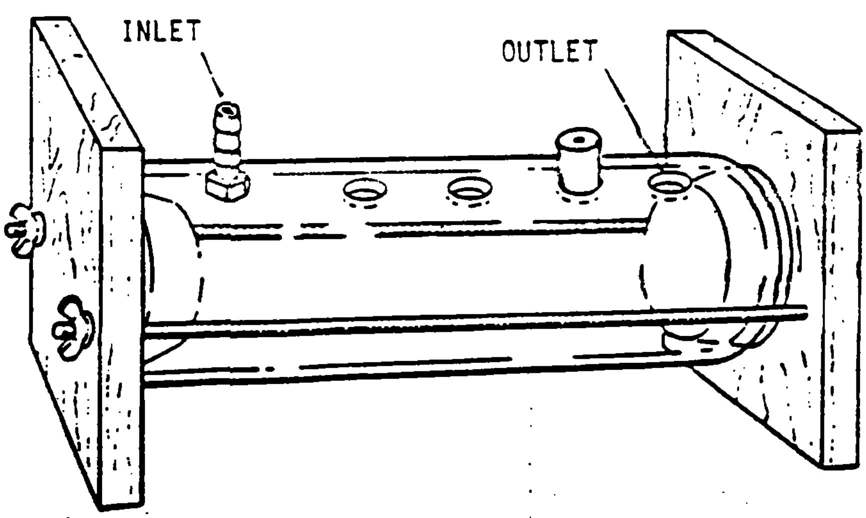


Figure 3. Flow-Through Stabilization Chamber

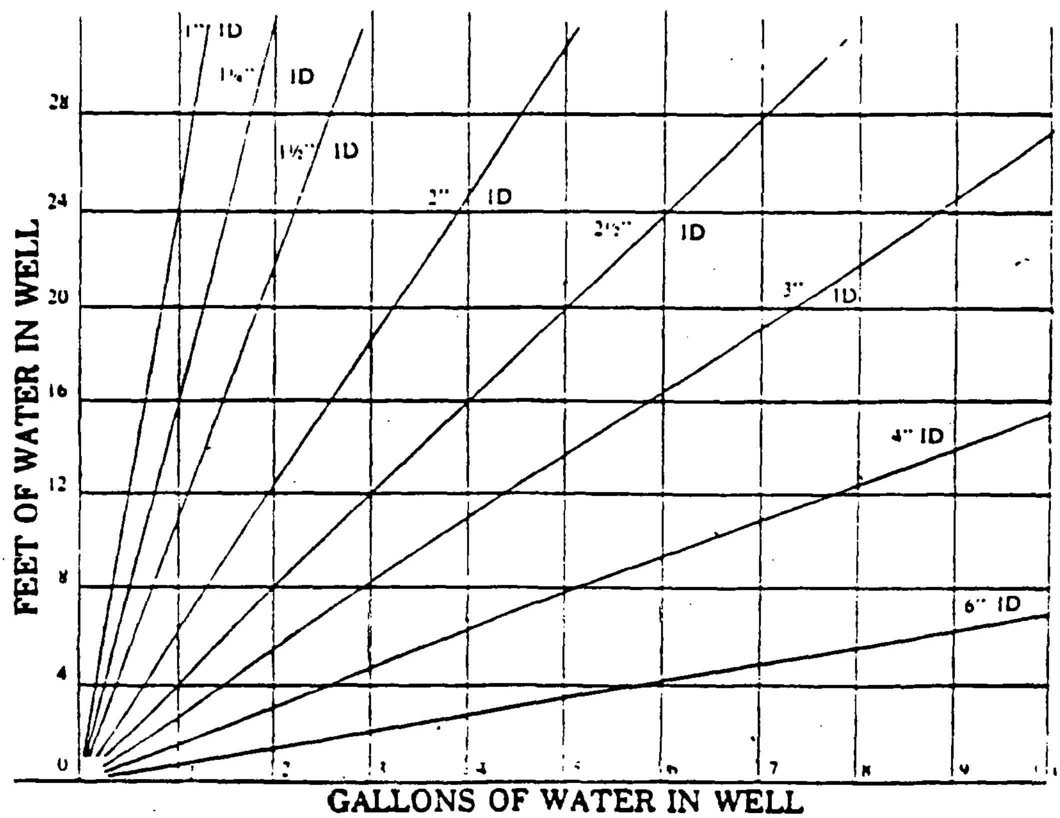
The results of the initial stabilization test should be recorded as suggested in Figure 4 and submitted to the Agency along with the well log and well construction details. If sampling methods change, the stabilization test should be repeated using the new equipment.

In some cases, it may be necessary to install wells in fairly tight (low transmissivity) formations which do not have sufficient yields to allow a stabilization test. For such wells, it is permissible to substitute a recovery rate test for the stabilization test. A recovery rate test is performed by taking initial measurements at the well of water elevation, pH, temperature and conductance; fully and as quickly as possible evacuating the well; measuring the water level as it recharges over time; and taking final measurements of water elevation, pH, temperature and conductance.

Figure 5 below provides a handy conversion for determining the volume of water in a well for various casing diameters.

Samples are collected as the well refills, not to exceed two hours after evacuation. For more information on interpreting results from a recovery rate test, see the section in Freeze, 1979 on the interpretation of slug test data. A suggested format for reporting the results is given in Figure 6.

Figure 5. Water in Storage



-meter	Foot of Casing
1 1/4"	0.0625
2"	0.163
4"	0.653
6	1.47
8	2.61
12"	5.87

Figure 4

STABILIZATION TEST

Site ______________

Date ______________

Well number ______________

Pumping rate (gallons/minute) ______________
Type of pump ______________
Water level before pumping (nearest 0.01 ft. below top of casing) ______________
Approximate well location ______________
Calculated volume of water in casing ______________
Weather conditions ______________

Time	pH (units)	Temperature-Corrected Conductance (umhos/cm)	Temperature (°C)	Water Level (nearest 0.01 ft.)	Cumulative Volume of Water Removed From Well (measured in gallons)

ENSR

WELL NO. ____________

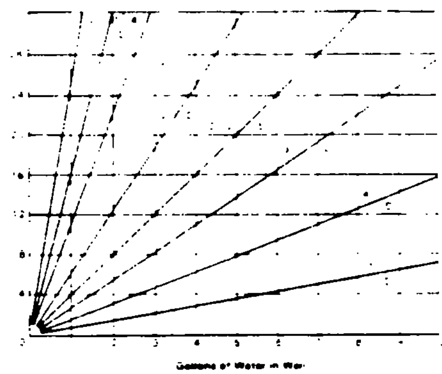
GROUND WATER SAMPLE COLLECTION RECORD

Project No. ____________ Date ____________ Time: Start ____________ am/pm

Project Name ____________ Finish ____________ am/pm

Location ____________

Weather Conds.: ____________ Collector ____________



1. WATER LEVEL DATA: (measured from ToC)

a Total Well Length ____________ Well Casing Type ____________

b Water Table Depth ____________ Casing Diameter ____________

c Length of Water Column ____________ (a-b)

c Calculated Purgeable Volume ____________

2. WELL PURGEABLE DATA

a Purge Method ____________

b. Required Purge Volume (@ ________ well volumes) ____________

c Field Testing: Equipment Used ____________

Volume Removed	T°	PH	Spec. Cond.	Color	Other

3. SAMPLE COLLECTION: Method ____________

Container Type	Preservation	Analysis Req

Comments ____________

M880244

Figure 6

Site	
Date	
Well number	

RECOVERY RATE TEST

Water level before evacuation (nearest 0.1 ft. below top of casing) ________
Approximate well location ________________________________
Weather conditions ________________________________

Initial: pH (units) ________
Conductance (umnos/cm*) ________
Temperature (°C) ________

Recharged: pH (units) ________
Conductance (umhos/cm*) ________
Temperature (°C) ________

Time From Evacuation	Water Level (nr. 0.1 ft.)	Calculated Recharge Rate ($\frac{\text{volume}}{\text{time}}$)

The test is finished when the water level has recovered to its pre-evacuation level.

*Conductance should be temperature-corrected to 25°C.

Monitoring Well Maintenance

A damaged or improperly constructed monitoring well can provide a conduit for contaminants to enter the ground water. In addition, monitoring data is most meaningful when it comes from repeated testing of the same well by the same methods under the same conditions. Therefore it is important that wells be maintained in good condition. Wells which are allowed to deteriorate and no longer provide suitable samples must be replaced.

Surface seals must be intact to prevent surface water entering the borehole. Obstructions in the well should be removed. Any well which cannot be sampled must be abandoned in accordance with the Minnesota Water Well Construction Code. If a well is lost, such as those accidentally buried by landfill equipment, excavations must be made to locate the well, so that it can be reconstructed or abandoned. Locking caps are necessary to prevent vandalism. Wells in vulnerable locations should be inspected weekly for damage.

Sample Collection from Monitoring Wells

Samples must be carefully and precisely collected. To assure that samples are taken correctly, appropriately trained laboratory personnel or consultants should collect the samples.

There is a wide selection of methods for collecting water samples from monitoring wells. Each method has advantages and disadvantages. The choice of method should be based upon well construction, the amount of water to be removed and the parameters of interest. Following is a discussion of several methods.

Squeeze or Bladder Pumps:

The major components of these systems include a collapsible bladder inside a long, rigid housing, a compressed gas supply and appropriate control valves. Water enters the bladder through the foot valve when the pump is submerged. Gas pressure is applied to the annular space between the rigid housing and the membrane, forcing the water up. The top check valve keeps the sample in the discharge line when the pressure is released, and more water enters the bladder through the foot valve.

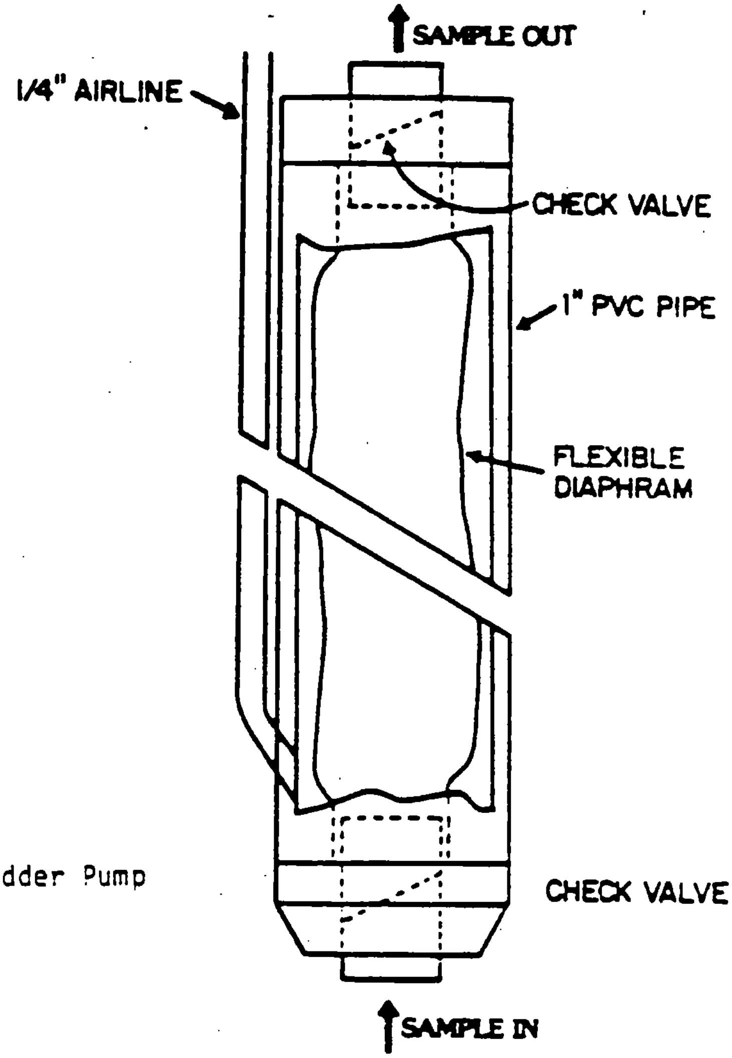


Figure 7. Squeeze or Bladder Pump

Advantages:

- -wide range of pumping rates
- -may be constructed of materials inert to the parameters of interest
- -no gas-water contact; no out-gassing, stripping or loss of volatiles
- -can be used well diameters as small as one inch
- -portable, or may be used as a dedicated installation
- -can be used to sample as deep as 200 feet

Disadvantages:

- -large gas volumes and long cycles needed for deep operation
- -pumping rate not as great as with submersible or suction pumps
- -control unit is relatively expensive

Usage Recommendations:

- -acceptable to use in most sampling applications
- -pump should be set above the screen for evacuation and sampling
- -attention must be given to adequate cleaning before each use to avoid cross-contamination of wells

Bailers:

Bailers can range in construction from a simple length of capped pipe on a rope to Teflon devices with a dual check-valve system used for sampling at discrete points in the water column. Wells are sampled by lowering the bailer to a given point in the water column and raising it, filled, to the surface.

Figure 8. Timco Variable-Capacity Discrete Point Sampler

Advantages:

- -few, if any, mechanical difficulties encountered in use
- -very portable; economical to build from easily obtainable parts
- -construction materials can be chosen for compatibility with the parameters of interest
- -can be built to fit small diameter wells
- -low surface-to-volume ratio reduces loss of volatile components
- -can be easily laboratory cleaned and taken into the field sealed to keep clean

Disadvantages:

- -requires much manual labor if used for well evacuation
- -difficult to fill sample bottles without aeration of samples unless the bailer is equipped with a bottom emptying device
- -the large amount of handling of the bailer needed in sampling can lead to increased risk of sample contamination

Usage Recommendations: (from Gibb, 1981)

- -the bailer should be constructed of a noncontaminating material (such as stainless steel or Teflon)
- -a pass-through type valve should be used to minimize disturbance as the bailer is lowered through the water column
- -the bailer should be lowered to the same depth (the top of the well screen) every time to create the same effect as pumping with a peristatic pump
- -bailing should be timed to approach a constant pumping rate and should continue until the appropriate well volumes are removed prior to collecting the sample
- -the rope used to operate the bailer should be of a nylon, polyester, or Teflon-coated material and should be held off the ground during the bailing process
- -the bailer and down-hole rope should be thoroughly cleaned (at least rinsed with distilled water) before use in each well

Submersible Pumps:

A submersible pump consists of a stack of impellers, driven by a special motor designed for use under water. This type of pump is appropriately used in wells with large volumes of water, wells with large water columns and deep wells. Submersibles can be used as portable pumps or permanently installed.

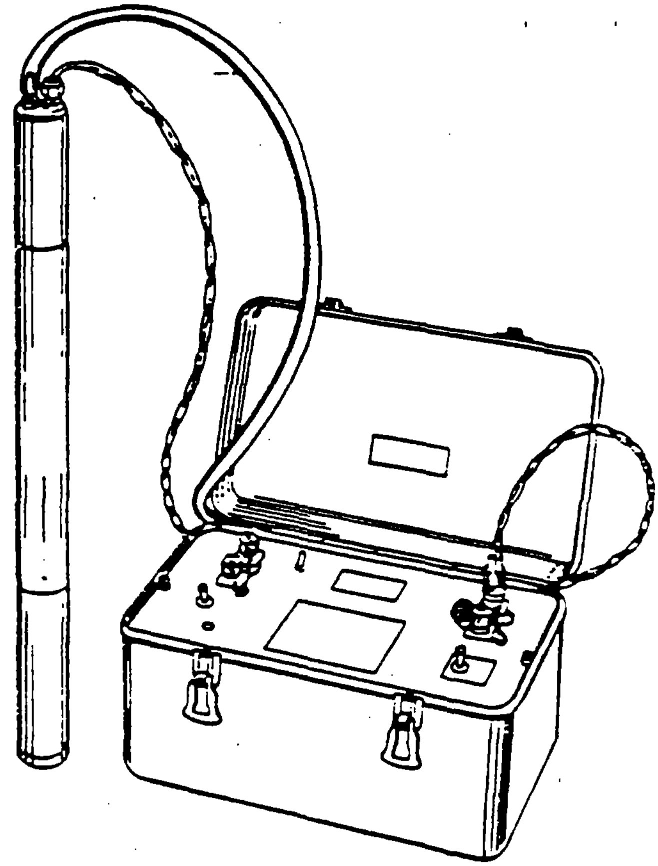


Figure 9. Johnson-Keck 2" Submersible Pump

Advantages:

- high pumping rates allow rapid evacuation and facilitate sampling
- can be used effectively at any depth applicable in Minnesota
- do not need to be primed
- permanently installed units eliminate risks of cross-contamination in sampling

Disadvantages:

- "portable" units require use of a truck or four-wheel drive vehicle to transport the pump and generator to the sampling site (not true for 2" submersibles)
- agitation of the sample may lead to the loss of volatile components (not true for pumps using a non-air-contact lift system)
- commonly available pumps require at least four-inch diameter wells; pumps for two-inch wells available from only a few suppliers at present
- sample contact with pumping mechanism may affect water quality

Usage Recommendations:

- care should be taken when using portable systems to ensure that all parts that contact the sample are cleaned before sampling each well
- the pump should be set above the well screen for evacuation and sampling
- permanent installation should not be made in areas where water contaminants will corrode the pump

Suction Lift Pumps:

Suction lift pumps are appropriately used where the water to be sampled is less than 25 feet deep and volatile components are not a concern. Types of suction-lift pumps include powered perstaltic and centrifugal pumps as well as hand-operated diaphragm and pitcher pumps.

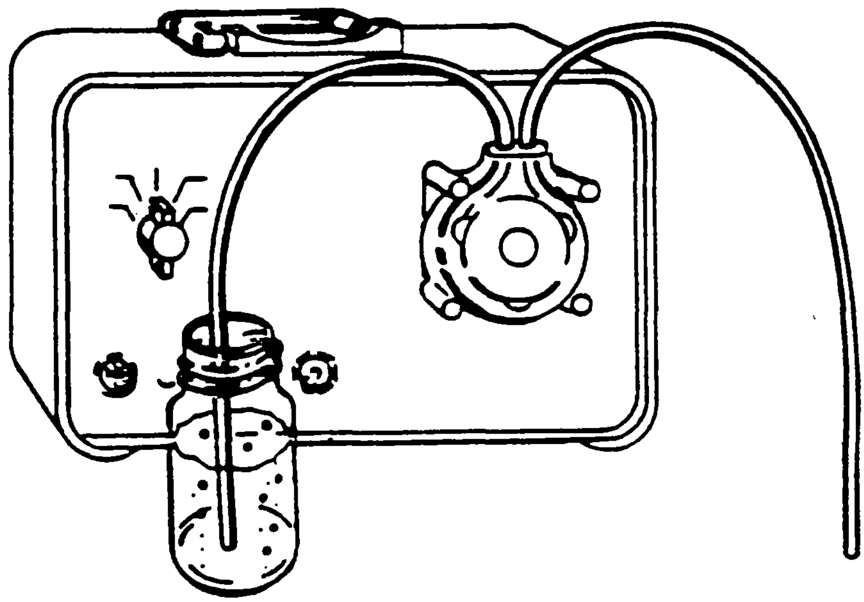


Figure 10. Masterflex Peristaltic Pump

Advantages:

- -many types made for field use
- -portable
- -relatively inexpensive
- -expedites sampling of small-diameter wells
- -fairly high pumping rates (all but peristaltics)
- -sample contacts only tubing, not pumping mechanism (peristaltic only)

Disadvantages:

- -cannot be used below the suction limit (20-30 feet of head)
- -suction and agitation may cause loss of dissolved gases
- -sample contacts pumping mechanism, which may cause changes in the parameters of interest (all types but peristaltics)

Usage Recommendations:

- -pump suction line should be set above the well screen for evacuation and sampling
- -peristaltic pumps should not be used when low (ppb) levels are to be determined
- -do not use where loss of gases and volatile components will affect the parameters of interest
- -new, cleaned tubing should be used for each sample

Air-Lift and Nitrogen-Lift Samplers:

These samplers operate by applying air pressure to a well or a sampling chamber to force a water sample out the discharge tube. This sampling technique is capable of withdrawing water from depths of at least 190 feet (Trescott and Pinder, 1970).

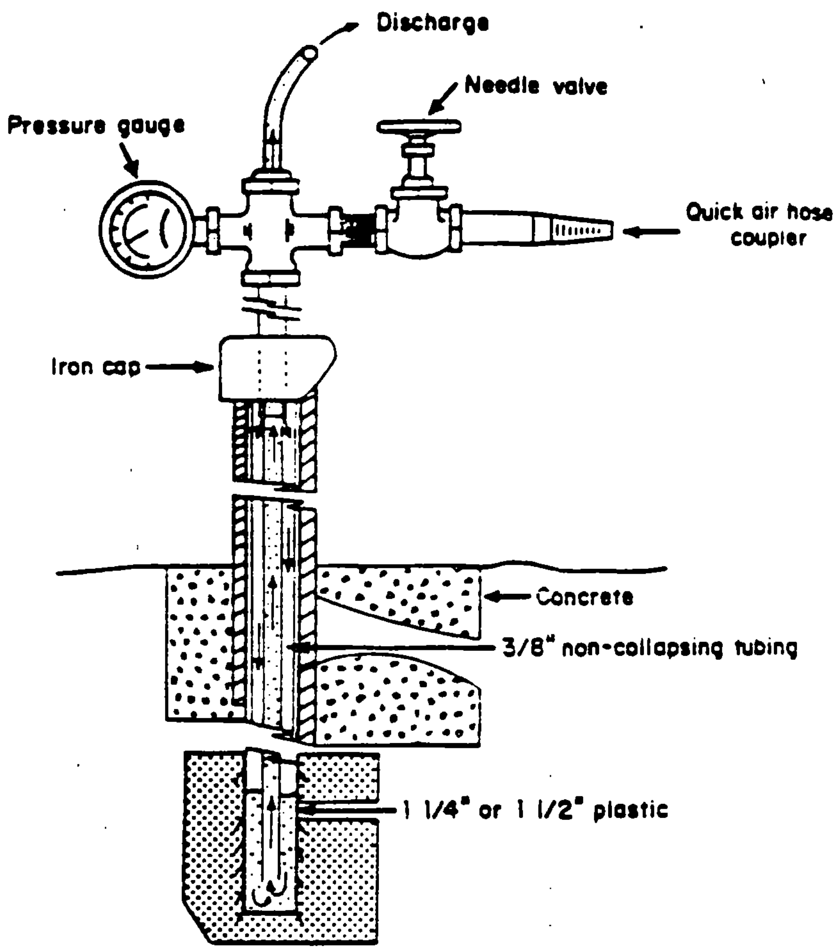


Figure 11. Air-Lift Sampler

Advantages:

-can be permanently installed, or used as a portable sampling device
-can be manufactured using easily obtainable parts

Disadvantages:

-repressurization releases dissolved CO_2 from solution, raising the pH, precipitating certain components and volatilizing others

Usage Recommendations:

-due to water chemistry changes caused using this sampling method, it is not generally recommended; those devices designed to prevent the air or nitrogen from escaping into the water in the well may be used for evacuation, with samples being taken afterward with a bailer
-when used as a portable device, care should be taken that all parts are clean prior to insertion into the well

SECTION 3

UNSATURATED ZONE MONITORING

Monitoring in the unsaturated zone may be pursued by either detection of seepage or by determination of the quality of the water seeping through the soil. Seepage detection may be of value only at sites designed for total containment systems, where any seepage constitutes a violation of permit conditions. Tensiometers, electrical resistance blocks, neutron logging or psychrometers may be used to detect seepage, triggering corrective actions aimed at eliminating any discharge from the site.

At facilities such as wastewater spray irrigation sites, the vegetation and soil are the treatment system and unsaturated flow comprising infiltration and percolation is part of the process. In these cases, samples of the soil moisture are collected and analyzed to provide information on the quality of the effluent reaching a particular depth in the soil profile.

Suction-cup lysimeters (Figure 12) are most commonly used to collect soil moisture samples although other types of lysimeters are also available. These sampling devices can be used in conjunction with monitoring wells to better define contaminant movement. Samples of the soil itself can also be analyzed for contaminants, although this is a more expensive procedure. In addition, geophysical methods such as electrical resistivity or electro-magnetic surveys may provide more information on changes in the unsaturated zone.

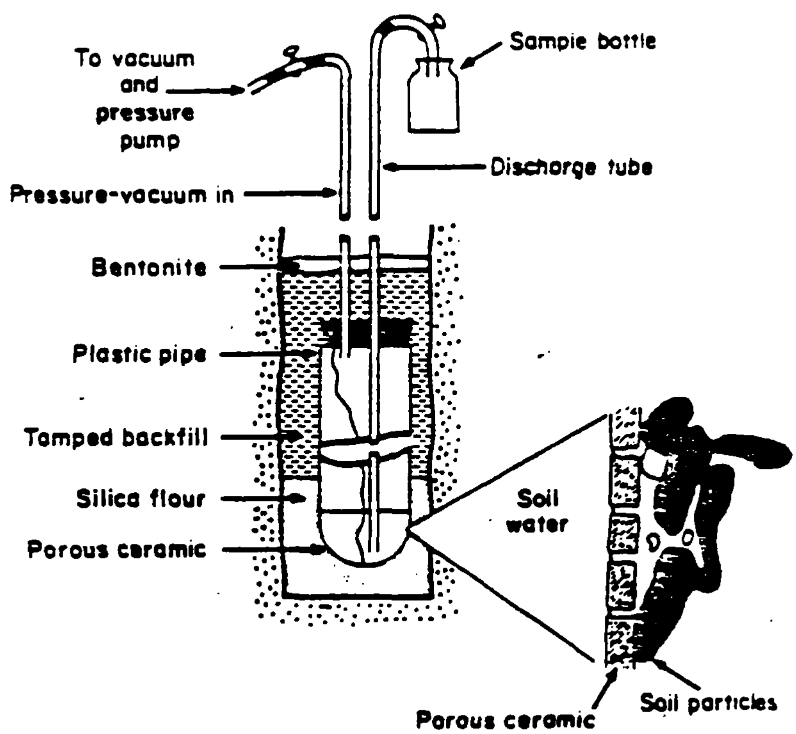


Figure 12. Suction-Cup Lysimeter

Locations for Lysimeters

Lysimeters should be placed in banks of two at each location to provide a larger volume of sample, to provide a backup system in case of failure of one of the units, and to provide a more representative sample. Both lysimeters in the bank should be installed in the same manner at the same depth. They should be placed approximately 2 feet apart.

One bank of lysimeters should be installed away from the potential contaminant source to provide background information. The others should be placed directly under the area to be monitored. For bottom-sealed sites, lysimeters should be located in the soil beneath the seal. For land disposal operations, the lysimeters should be placed in the soil under the waste area. Lysimeters should be placed below the crop root zone in spray fields.

Installation of Lysimeters

When installing suction-cup lysimeters it is important that certain details be given strict attention. These include:

- Porous ceramic samplers should be flushed with dilute acid and deionized water before use to remove contaminants left in the cup during manufacture. A vacuum should be applied to the assembled lysimeter and 250 to 500 ml. of 0.1N hydrochloric acid, followed by 500 ml. of deionized water, pulled through the ceramic wall and discarded. All parts should be completely rinsed with deionized water.

- Sampling tubes must be clearly marked with the lysimeter number as well as their purpose (sampling or vacuum) so that once they are installed, no errors will be made as to their designation.

- Assembled lysimeters should be soaked in deionized water immediately before installation so that all the pores in the ceramic cup are filled with water.

- The installation bore hole should be at least 2 inches wider than the lysimeter.

- It is essential that good contact be provided between the ceramic cup and the surrounding soil. This is best ensured by pouring enough fine silica flour slurry into the borehole to completely surround the cup, then pressing the cup firmly into the slurry.

- The bore hole should be slowly refilled with continuous tamping to eliminate any large voids. A plug of bentonite will aid in sealing off the lysimeter from direct surface infiltration.

- Surface soil should be mounded around the exposed sampling tubes, and a protective cover (such as a lockable metal box) placed over them.

- In most applications, lysimeters should not be placed within one foot of the seasonal high water table.

Sample Collection From Lysimeters

When sampling from lysimeters it is important not to apply high vacuum levels to the sampler. Some recommendations for sampling include:

-Vacuum application should be sufficient to collect enough sample for analysis. This will have to be determined on a trial-and-error basis, depending on moisture conditions, soil type, etc. A recommended starting period is one day in coarse textured soils and two days in medium to fine soils.

-Vacuum should be the lowest value that will allow sample collection, generally between 0.3 and 0.8 atmospheres (4.4 to 11.8 pounds per square inch); 0.8 atmospheric pressure usually works best for lysimeters installed with silica flour around the ceramic cup.

-The applied air pressure for sample expulsion should also be as low as possible, to avoid pushing most of the sample back out of the cup into the soil.

Lysimeter Maintenance

To facilitate collection of representative samples and maintenance of these devices, all lysimeters should have vacuums placed on them at a minimum of once a month with samples either wasted or analyzed according to monitoring requirements. Sample tubes should be clearly labeled at all times to eliminate confusion. Lysimeters should not be left under vacuum in extremely cold weather to prevent damage from freezing.

SECTION 4

SURFACE WATER MONITORING

Identifying Surface Water Monitoring Points

Surface water is monitored in instances where contaminated ground water may potentially discharge into surface water. If the surface water affected is a river or stream, monitoring should take place upstream and downstream from the waste facility and at the point of discharge. Standing bodies of water should be monitored at the apparent point of discharge and at apparently unaffected points as well. A stake or permanent marker should be placed on the bank to mark routine monitoring locations. Care should be exercised in selecting sampling points so that all possible impacts on the stream or lake are noted. For example, downstream samples for a landfill should not extend past an outfall for another discharger or ambiguous data may be generated.

A surface water monitoring plan should also be submitted to the Agency for approval prior to initiating sampling. The Agency will review the plan for completeness and appropriateness of parameters and sampling frequency.

Sampling Surface Waters

When samples are collected from a river or stream, water quality may vary with depth, stream flow, distance from shore and from one shore to the other. It is best to take an integrated sample from top to bottom in the middle of the stream. VanDorn or Kemmerer samplers can be used for this purpose. Instructions on their use are included in Appendix B.

When sampling shallow water (less than 3 feet deep), it is best to take a grab sample in the middle of the stream at mid-depth, holding the sample container under the surface until filled. The mouth of the container should face into the flow.

Sampling extremely shallow water, such as leachate seeps, can be very difficult. Care must be taken not to disturb the bottom sediments when sampling. If the site is a routine monitoring point, a small depression should be made to allow more water to collect for sampling. A carefully-held peristaltic pump sampling tube can then be used to collect the sample.

In shallow streams the sampling should start at the furthest downstream point and move upstream so that any disturbances caused by sampling do not affect the quality of the water sampled. In deeper waters such as rivers, sampling is usually done from boats or bridges, so the disturbance is minimal. For such cases, sampling should begin first at the upstream point, next to the downstream point, and finally to the sample point closest to the apparent source of discharge. In that way, the chance of contaminants clinging to the sampler is reduced.

SECTION 5

SAMPLING FROM WATER SUPPLY WELLS

When samples are required to be drawn from wells used as drinking or industrial water supplies, the following procedure should be followed:

- Samples should be taken from the point closest to the well, before the water is softened, filtered or heated.

- If possible, samples should be taken before the water enters the pressure tank. If that is not possible, let the water run to waste long enough to empty the tank and the water in storage in the pipes.

- Obtain well logs, or where not available, find out from the well owner construction details of the well, including completed depth, static water level and well diameter. This will allow the amount of water in storage in the casing to be determined. If the well is in current use, evacuation of one well volume (and the pressure tank) should be sufficient to obtain a sample of fresh aquifer water. If the well has not been used recently, a stabilization test should be performed to determine the amount of pumping necessary.

- Remove aerators, filters, or other devices from the tap before sampling.

- In some cases, it is desirable to obtain a sample of the water which represents the quality of the water which is being consumed. For this, the tap sampled should be the one most frequently used for drinking and cooking. Only is this instance is it proper to leave aerators, filters, etc. on the tap when the sample is being drawn.

SECTION 6

SAMPLING FOR ORGANICS

When sampling for volatile organics, samples should be obtained with a Teflon bailer. Wells must be properly evacuated (see stabilization tests, page 6) before sampling. Other methods of water removal may be used for the initial evacuation. Stainless steel bailers are less desirable because some organics may be absorbed by metal (Pettyjohn, 1981). The sample vials should be overfilled without entrapped air bubbles to achieve a positive meniscus, shown in Figure 13. Bottom-emptying devices on bailers will aid in sample transfer without aeration. Teflon bailers are also appropriate for obtaining grab samples for other organic compounds such as pesticides, PCB's, etc.

It is important that the well be properly evacuated prior to sampling, although any of the pumps described earlier (hexane and distilled water rinsed) can be used for that purpose. Where adequate analytical sensitivity and sample uniformity cannot be obtained by grab sampling, continuous sampling procedures are used to concentrate and recover non-volatile organic constituents from relatively large volumes of ground water. Descriptions of these procedures are available (Pettyjohn, 1981; Scalf, 1981).

Figure 13. Filled Vial for Volatile Organics

SECTION 7

FIELD MEASUREMENTS AND SAMPLE PREPARATION

Prior to evacuating the well, depth to ground water should be measured to the nearest hundredth of a foot (0.01 foot). Depth to water must be reported relative to the top of the well casing as well as the calculated water surface elevation. Weighted steel tapes are preferred for depth measurement, but other methods may be used if the desired accuracy can be obtained.

A stabilization test should be performed for each monitoring well to determine the amount of pumping required to obtain a sample of water from the formation. Section 2 of this manual discusses the stabilization test procedure in greater detail. Each well should be pumped at the rate used in the stabilization test for the period of time which was required to obtain stabilized readings. Once the well has been thus evacuated, a sample should be drawn for field analyses of pH, temperature, and specific conductance. Manufacturers' directions for usage of the pH and conductance meters should be followed. Calibration of the meters should be performed daily.

Another sample should be taken for laboratory analysis. Sample containers should be supplied by the laboratory. The container should indicate the types of analyses to be performed. Field filtration through a 0.45 micron filter should be done on that portion of the samples to be analyzed for dissolved metals. A new filter should be used for each sample, and the filtration apparatus should be cleaned between sample locations. Appropriate preservation techniques must be followed immediately upon sample collection (and after filtration for dissolved parameters) to minimize chemical changes which could affect analytical results. Appendix C shows the appropriate container types and preservation methods for various parameters.

The same field analysis, filtration, and preservation techniques should be observed for all types of samples, except that samples taken from drinking and industrial water supply wells should not be filtered. By not filtering, the analysis will show the concentration of metals in the water as it is being consumed.

All samples should be iced or refrigerated and transported to the laboratory within 24 hours of sampling. To assure prompt analysis, it is advisable to sample early in the week so that samples do not remain in the laboratory over the weekend.

SECTION 8

ESTABLISHING A SAMPLING PROTOCOL

A sampling protocol for each site should be established, maintained by the site owner/permittee, and made available to field personnel before each anticipated sampling date so adequate preparation can be made. The protocol should include the following:

- the order in which the wells and other monitoring points are to be sampled (it is generally preferable to begin with the wells containing the best quality water and end with those with the worst to lessen the chance of cross-contamination);

- methods to be followed at each sampling point, including the stabilization procedures;

- equipment to be used for water level measurement, evacuation, and sampling;

- procedures to be followed for cleaning the equipment between samples;

- the type of containers to be filled and the volume of sample needed for each;

- field testing, filtration, and preservation methods;

- the cleaning procedure and volume and type of cleaning agent to be used for cleaning the equipment between sampling points; and

- sample shipping procedures or procedures to be followed when samples are delivered to the laboratory, as appropriate.

A copy of the protocol should be kept in a field notebook. The notebook should also include accurate records of measurements, notes and comments made at each sampling event. In the Procedures Manual for Ground Water Monitoring at Solid Waste Disposal Facilities (USEPA, 1977), USEPA recommends that the following records be kept for each sample submitted to the laboratory:

- sample description--type (ground water, surface water), volume;

- sample source--well number, location;

- sampler's identity--chain of evidence should be maintained; each time transfer of a sample occurs, a record including signatures of parties involved in transfer should be made;

- time and date of sampling;

- significant weather conditions;

-sample laboratory number;

-pertinent well data--depth of well, depth to water table, water surface elevation, and schedule and method of pumping;

-sampling method--vacuum, bailer, pressure;

-type and number of preservatives, if any (e.g., NaOH for cyanide, H_3PO_4 and $CuSO_4$ for phenols, etc.), or whether the sample was filtered;

-sample containers--type, size, and number (e.g., three liter glass stoppered bottles, one gallon screw-cap bottle, etc.);

-reason for sampling--initial sampling of new landfill, annual sampling, quarterly sampling, special problem sampling in conjunction with contaminant discovered in nearby domestic well, etc.;

-appearance of sample--color, turbidity, sediment, oil on surface, etc.;

-any other information which appears to be significant--(e.g., sampled in conjunction with state, county, local regulatory authorities; samples for specific conductance value only; sampled for key indicator analysis; sampled for extended analysis; resampled following engineering corrective action, etc.);

-name and location of laboratory performing analysis;

-water temperature upon sampling;

-thermal preservation--(e.g., transportation in ice chest);

-analytical determinations (if any) performed in the field at the time of sampling and results obtained--(e.g., pH, temperature, dissolved oxygen, and specific conductance, etc.);

-analyst's identity and affiliation.

SECTION 9

LABORATORY REQUIREMENTS

All analyses must be performed according to USEPA approved methods listed in Methods for Chemical Analysis of Water and Wastes, or The Determination of Halogenated Chemicals in Water by the Purge and Trap Method (USEPA Method 502.1) and The Analysis of Aromatic Chemicals in Water by the Purge and Trap Method (USEPA Method 503.1), or equivalent methods approved by USEPA. Each laboratory doing Agency-required analyses will be asked to provide the Agency with a list of methods referenced to the above documents, for all required tests.

Samples should ideally be collected by laboratory personnel. In all cases, sample containers must be provided by the laboratory. Due to the sensitivity of analyses for volatile organic compounds, it is recommended that these samples in particular be collected by experienced field or laboratory personnel only. The laboratory must have a quality assurance procedure for sample containers. The containers should be of the types specified in Appendix C. Preservatives and instructions for their use should also be provided.

The Agency is now requiring that a quality assurance plan for each site be approved before sampling begins. These plans must not only be submitted for new sites, but also for each change of laboratory at existing sites. Plans must be kept current, with the Agency notified of any change or variation in procedure. A quality assurance program is now being developed for many MPCA programs. Contact Orbbie Webber (MPCA, Solid and Hazardous Waste Division) for more information.

The following list of items must be included in a quality assurance plan:

- the order in which the wells are to be sampled and the rationale for this order;

- the amount of water in gallons and well volumes which must be evacuated from each well prior to sampling based on stabilization tests or other methods; if other methods are used, they should be detailed;

- a list of the parameters to be analyzed for in each well, a sampling schedule, and a parameter protocol;

- the methods followed and equipment used for measuring the static water level, stabilizing the well, evacuating each well, obtaining a sample, and field filtering;

- the cleaning procedures, and materials and volume of cleaning agent used for cleaning equipment between wells;

- sample preservation methods, minimum sample volumes and container specifications for each parameter;

- a sample chain-of-custody form which will be used;

-shipping and handling procedures and a time schedule from the field to the laboratory to actual analysis for each parameter;

-the methods to be used for analysis, referenced to EPA or Standard Methods;

-the lowest detection limits and reporting limits which are achieved according to the method and equipment used;

-the type of equipment used in the laboratory and its maintenance schedule;

-the number of quality control samples (blanks, spikes, or duplicates) that are proposed to be analyzed as a part of each sample set for the parameters to be analyzed in the investigation; at least one field blank must be analyzed and reported for each sample set for volatile organics analyses; and

-the scheduled first sampling date so that Agency staff has an opportunity to split samples, inspect the wells, and observe the sampling procedure with the person assigned to collect the samples.

Field checks should be performed for purposes of quality assurance. In USEPA's Handbook for Analytical Quality Control in Water and Wastewater Laboratories (March, 1979), the following checks are recommended:

-Duplicate Samples - At selected stations on a random time frame duplicate samples are collected from two sets of field equipment, or duplicate grab samples are collected. This provides a check of sampling method and equipment for precision.

-Split Samples - A representative subsample from the collected sample is removed and both are analyzed for the pollutants of interest. The samples may be reanalyzed by the same laboratory or analyzed by two different laboratories for a check of the analytical procedures.

-Spiked Samples - Known amounts of a particular constituent are added to an actual sample or to blanks of deionized water at concentrations at which the accuracy of the test method is satisfactory. The amount added should be coordinated with the laboratory, and the person performing the spike must be proficient in qualitatively performing the operation. This method provides a proficiency check for accuracy of the analytical procedures.

-Sample Preservation Blanks - Acids and chemical preservatives can become contaminated after a period of field use. The sampler should add the same quantity of preservative to some distilled water as normally would be added to a water sample. This preservative blank is sent to the laboratory for analysis of the same parameters that are measured in the sample and values for the blank are then reported along with the sample values. Chemical preservatives should be changed every two weeks, or sooner, if contamination increases above predetermined levels.

-Field Blanks - Field blanks may be necessary where sampling equipment or other factors could affect the parameters of interest. Field blanks consist of deionized water, run through clean sampling equipment, then preserved and handled in the same manner as the samples.

"Chain of custody" tracking is recommended for all samples. The following discussion of this procedure is from the Procedures Manual for Ground Water Monitoring at Solid Waste Disposal Facilities (USEPA, 1977).

Proper chain of custody procedures play a crucial role in enforcement cases. The following are some basic guidelines which have legal significance:

-As few people as possible should handle the sample.

-Stream and ground water samples should be obtained by using standard field sampling techniques as discussed in this manual.

-The chain of custody records should be attached to the sample container at the time the sample is collected, and should contain the following information: sample number, date and time taken, source of the sample (include type of sample and name of firm), the preservative and analysis required, name of person taking sample, and the name of any witness. The prefilled side of the card should be signed, timed, and dated by the sampler. The sample container should be sealed, with an indication of the regulatory agency's designation, date, and sampler's signature attached. The seal should cover the string or wire tie of the chain of custody record, so that the record or tag cannot be removed or the container opened without breaking the seal. The tags and seals should be filled out in legible handwriting. When transferring the possession of samples, the transferee should sign and record the date and time on the chain of custody record. Custody transfers, if made to a sample custodian in the field, should be recorded for each individual sample. The number of custodians in the chain of possession should be as few as possible. If samples are delivered to the laboratory when appropriate personnel are not there to receive them, the samples should be locked in a designated area within the laboratory so that no one can tamper with them.

-Blank samples should be collected in containers with or without preservatives, so that the laboratory analysis can be performed to show that there was no container contamination.

-A field book or log should be used to record field measurements and other pertinent information necessary to refresh the sampler's memory if he later becomes a witness in an enforcement proceeding.

-A separate field notebook should be maintained for each facility. It must be stored in a safe place where it can be protected and accounted for at all times. A standard format should be established to minimize field entries. The entries should then be signed by the field sampler. The responsibility for preparing and retaining field notebooks during and after a sampling survey should be assigned to a survey coordinator or his designated representative.

-The sampler is responsible for the care and custody of the samples collected. He must assure that each container is in his possession or in his view at all times or stored in a locked place where no one can tamper with it.

-Photographs can be taken to establish exactly where the samples were obtained. Written documentation on the back of the photograph should include the signature of the photographer, the time, date, and site location. Photographs should be handled according to the established chain of custody procedures.

-Each laboratory should have a sample custodian to maintain a permanent log book in which he records for each sample: the person delivering the sample, the person receiving the sample, date and time received, source of sample, sample number, how the sample was transmitted to the lab, and a number assigned to each sample by the laboratory. A standardized format should be established for log-book entries. The custodian should insure that heat-sensitive or light-sensitive samples or other sample materials having unusual physical characteristics that may require special handling are properly stored and maintained. Distribution of samples to laboratory personnel who are to perform analyses should be made only by the custodian. The custodian should log the laboratory sample number, time, date, and the signature of the person to whom the samples were given. Laboratory personnel should examine the seal on the container prior to opening and should be prepared to testify that their examination of the container indicated that it had not been tampered with.

Figure 14 shows a chain-of-custody form currently in use by the Agency. The form is a multi-part carbonless form, with copies distributed to the sampler, laboratory and regulatory agency.

Minnesota Pollution Control Agency
Solid Hazardous Waste Division
1935 West County Road B2
Roseville, Minnesota 55113

S 05006

Figure 14. Chain of Custody Form

CHAIN OF CUSTODY RECORD

Project Name										Name of Sampler	
Field Number	Date	Time	Sample Type(s)						Sample Location	Analyses Requested	Comments on Samples
			monitoring well	existing well	surface water	wastewater	waste	other			

Remarks on Site

Samples Relinquished by	Samples Received by	Comments	Date/Time
Samples Relinquished by	Samples Received by	Comments	Date/Time
Samples Relinquished by	Samples Received by	Comments	Date/Time

Means of Delivery

Seals intact: ☐ YES ☐ NO ☐ N.A.

Original and yellow copies to lab. Pink copy to MPCA. Lab forwards completed yellow copy to MPCA with analytical results.
PQ-00343-01 (12/83)

SECTION 10

REPORTING REQUIREMENTS

The results of the required analyses are to be submitted to the Agency in the time frame specified in the permit, order, or agreement. Submittal of reports should be on forms provided by the Agency when so directed. Information to be reported includes brief descriptions of the following:

- the static water level for each well to the nearest 0.01 foot from the surveyed reference point;

- the volume of water removed before sampling;

- sampler's field comments on unusual or noteworthy occurrences during the sampling event;

- a statement explaining the reasons for and ramifications of any deviations in sampling or analysis techniques or equipment used from that stated in the approved quality control plan; and

- the laboratory results of each sample analysis along with quality control sample analyses (i.e., blanks, spikes, duplicates). An analysis of a field blank for each sampling event for volatile organics must be included.

Annual reports may also be required. These should cover one calendar year and be submitted by the end of the following January. In the annual report, the facility owners or operators provide the Agency with a detailed interpretation of the monitoring results collected from each site. These reports are to be prepared by persons knowledgeable in the field of ground water pollution. In many cases, this will require the disposal site permittee to retain the services of a qualified consultant to prepare the report. Contents of the report should include:

- a narrative, describing the effects which the site is exerting on surrounding ground water quality and any changes made or maintenance needed in the monitoring network;

- data summary tables;

- local rainfall conditions at the closest measurement station (information obtainable from the National Climate Data Center, Federal Building, Asheville, North Carolina 28801; 704-259-0682);

- well hydrographs for water elevations at all monitoring points; and

- graphics showing concentration versus time for all measured parameters, by well, for as long as the record exists. It is unnecessary to graph parameters consisting of only one data point per year or those which are consistently reported as below detectable limits.

APPENDIX A:

SAMPLING FREQUENCY; AND
SITE-TYPE GUIDELINES FOR MONITORING:

1. Community drainfields
2. Hazardous waste facilities
3. Land application sites
4. Landfills:

    a. Mixed municipal waste (sanitary) landfills
    b. Industrial waste landfills
    c. Demolition waste landfills

5. Rapid infiltration basins
6. Spill sites
7. Surface impoundments

Monitoring systems should be individually designed, taking into account a site's hydrogeologic setting. Each site will have monitoring requirements established by permit or by letter of permit amendment, giving monitoring point locations, sampling frequency, and required parameters. Monitoring systems should be designed to provide the information necessary to effectively evaluate any impacts which the facility may exert upon the ground water. For more information on the design of monitoring systems to meet Agency requirements, see "Guidelines for Ground Water Monitoring System Design" (MPCA, 1985).

The remainder of this appendix lists general guidelines for ground water monitoring at various types of waste management facilities in terms of required parameters and sampling frequency. Ideally, sampling should be timed to coincide with the spring thaw, the summer peak of evapotranspiration, and the autumn dry season prior to freeze-up. This manual takes a new approach, by dividing the State into sampling regions and specifying a seasonal monitoring schedule for each region. The regions are shown in Figure A-1, and the schedule given in Table A-1. Facilities with year-round hydraulic loading, such as community drainfields, will still be required to adhere to a quarterly monitoring schedule.

Table A-2, which appears at the end of this appendix, provides a summary of monitoring parameters for various waste management facility types.

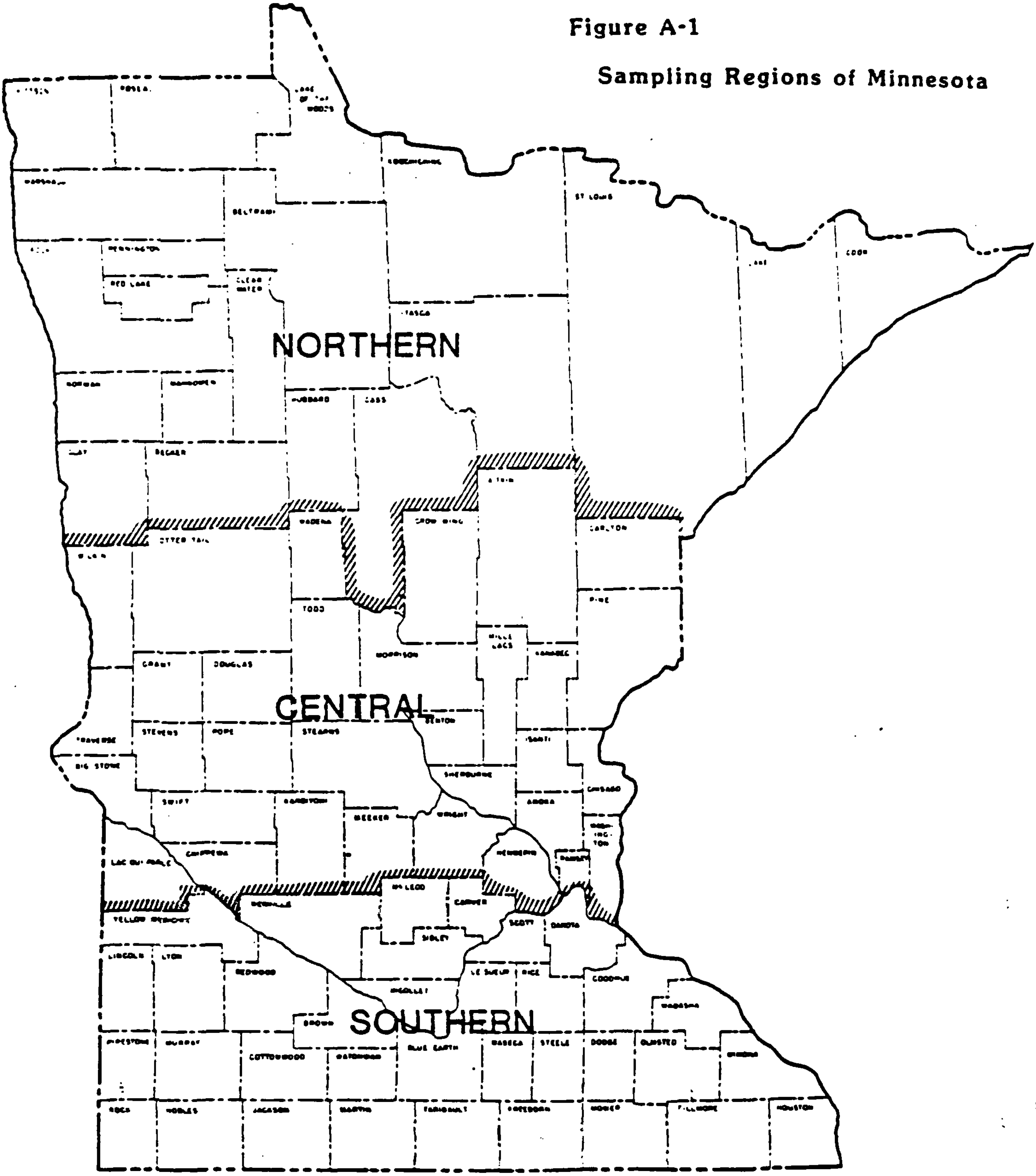
Table A-1

Monitoring Schedule for Seasonal Frequency

	Spring	Summer	Autumn
Southern 1/3	March 14-April 21	June 21-July 31	October 21-November 21
Central 1/3	March 28-April 28	July 1-August 7	October 14-November 14
Northern 1/3	March 28-May 14	July 1-July 31	October 1-October 31
Submit Reports By	July 31	October 31	With Annual Report by January 31

Figure A-1

Sampling Regions of Minnesota



COMMUNITY DRAINFIELDS

Large drainfields designed for loading rates greater than or equal to 5000 gallons per day must monitor ground water to meet Agency requirements. Those designed for loading rates less than 5000 gallons per day and greater than 1200 gallons per day will be required to monitor if a case-by-case review of the system shows it to be necessary. Also, if a land development project proposed on-site systems which individually were less than 1200 gallons per day but with a cumulative loading over a given area which would be equivalent to a larger system, then the combined effects of that project would also need to be evaluated.

Monitoring systems should be designed to provide the information necessary to effectively evaluate any impacts which the system may exert upon the ground water. For more information on the design of monitoring systems to meet Agency requirements, see "Guidelines for Ground Water Monitoring System Design" (MPCA, 1985). A detailed guidance manual on community drainfields has also been prepared by the Agency, entitled "High Rate Soil Absorption System Task Force Final Report" (MPCA, 1984).

Samples should be collected in the months of March, June, and September by the methods described in this manual. Parameters to be analyzed include:

Alkalinity
Chemical Oxygen Demand
Chloride
Fecal Coliforms
Hardness
Influent Flow
Inspection Pipe Observation
Nitrogen, Ammonia
Nitrogen, Kjeldahl
Nitrogen, Nitrate
pH(1)
Specific Area of Application
Specific Conductance(2)
Sulfate
Temperature(2)
Volatile Organics
Water Elevation(3)

(1) Two measurements: in field, immediately after obtaining sample and in laboratory.
(2) As measured in field.
(3) As measured in field before pumping or bailing.

Analyses should be done in accordance with the requirements of this manual, pages 25-30.

In the event that the system is no longer used, monitoring should continue on a quarterly basis for at least one year, when the Agency will evaluate the need for continued monitoring. If no serious impacts are detected, monitoring may cease at that time. All wells should be abandoned in accordance with the Minnesota Water Well Construction Code when monitoring ceases.

HAZARDOUS WASTE FACILITIES

Environmental monitoring is critical at hazardous waste facilities. For that reason, the rules governing hazardous waste management are very specific regarding monitoring. Federal requirements are presented in 40 CFR Parts 264 and 265 (Federal Register, Volume 47, Number 143, July 26, 1982) and State of Minnesota requirements in Minnesota Rules Chapter 7045 distributed by the Department of Administration, Documents Section, 117 University Avenue, St. Paul, Minnesota 55155.

Ground water monitoring design, construction and implementation at uncontrolled hazardous waste sites is subject to review by the Agency. Procedures for monitoring uncontrolled sites are determined on a case-by-case basis. Contact the Agency for additional information.

LAND APPLICATION SITES

Minnesota Rule Chapters 7040.0100-7040.4700 regulates the landspreading of municipal sewage sludge. If sewage sludge is applied to land which is owned, leased, or rented by the political subdivision generating the sludge (classified a landspreading facility), ground water monitoring may be required. The rules specify the background parameters to be analyzed for and the depth and location of monitoring wells. Sampling frequency and analytical parameters will be determined on a case-by-case basis.

Monitoring at land application facilities for effluents is determined by the hydraulic loading rate. In general, systems where hydraulic loading rates are based on either crop irrigation requirements (consumptive use) or nitrogen requirements will not be required to monitor ground water. Exceptions to this generality would be systems located on extremely coarse soils, over shallow ground water, or close to downgradient drinking water wells, or if the wastewater contains a parameter at a concentration which may impact ground water use.

Land application facilities which apply wastewater in excess of crop irrigation and nitrogen requirements will be required to monitor ground water. Monitoring systems should be designed to provide the information necessary to effectively evaluate any impacts which the system may exert upon the ground water. For more information on the design of monitoring systems to meet Agency requirements, see "Guidelines for Ground Water Monitoring System Design" (MPCA, 1985). Minimum monitoring parameters include:

Ammonia Nitrogen
Chloride
Nitrate + Nitrate Nitrogen, as N
pH(1)
Specific Area of Application
Specific Conductance(2)
Water Elevation(3)

(1) Two measurements: in field, immediately after obtaining sample and in laboratory.
(2) As measured in field.
(3) As measured in field before pumping or bailing.

If the water table elevations are very deep at a land application site or if it is necessary to detect downward movement of specific wastewater components before they reach the water table, lysimeter installation may be required. The placement of lysimeters will be dependent on soil characteristics, crop rooting depth, water table elevation and behavior of parameters of concern in the soil environment.

At a minimum, sampling frequency for monitoring wells will be as described for seasonal monitoring described earlier in this appendix. More frequent sampling may be required based on hydraulic loading rates, length of spray season, soil permeability, ground-water flow direction, ground-water flow velocity and concentration of specific parameters of concern in the wastewater.

Post-operative monitoring should continue seasonally for two years after spraying is discontinued. At this time the Agency will reevaluate the monitoring program and make recommendations for either increasing or decreasing monitoring requirements. Following the initial post-closure reevaluation, monitoring should continue as directed by the Agency, or until one year of monitoring data shows no contamination (see page 5), whereupon monitoring may cease at the site. All wells should be abandoned in accordance with the Minnesota Water Well Construction Code when monitoring ceases.

MIXED MUNICIPAL WASTE (SANITARY) LANDFILLS (INCLUDING MODIFIED SANITARY LANDFILLS

All sanitary landfills in Minnesota are required to monitor ground water. Their monitoring systems should be designed to provide the information necessary to effectively evaluate any impacts which the facility may exert upon the ground water. For more information on the design of monitoring systems to meet Agency requirements, see "Guidelines for Ground Water Monitoring System Design" (MPCA, 1985).

New wells, including both those at new and existing facilities, should be sampled for the following parameters to establish the initial quality of the ground water.

Alkalinity	Manganese, Dissolved
Ammonia Nitrogen	Mercury, Dissolved
Arsenic, Dissolved	Nitrate + Nitrite, as N
Cadmium, Dissolved	pH(1)
Calcium, Dissolved	Potassium, Dissolved
Chemical Oxygen Demand	Sodium, Dissolved
Chloride	Specific Conductance(2)
Chromium, Total Dissolved	Sulfate
Copper, Dissolved	Suspended Solids, Total
Dissolved Solids, Total	Temperature(2)
Iron, Dissolved	Volatile Organics(4)
Lead, Dissolved	Zinc, Dissolved
Magnesium, Dissolved	Water Elevation(3)

(1) Two measurements: in field, immediately after obtaining sample and in laboratory.
(2) As measured in field.
(3) As measured in field before pumping or bailing.
(4) Halogenated and non-halogenated, purge-and-trap method.

One sampling event is not sufficient to establish background water quality. Seasonal variation, sampling variation, analytical variation and random error occur. Monitoring wells at new sites will be required to have three background samples. The first sample will require analysis of the extended list of parameters for each well. Within 30 days after this sample is taken the analytical results should be submitted to the Agency. At least two more background samples taken at one month intervals will be required for each well. However, based on the results from the first sampling round, the Agency may reduce the number of parameters required from the extended list or extend the intervals between sampling events. For new wells at existing or expanded sites, three samples analyzed for the extended list will be required to establish initial water quality. The sampling interval will be based on the purpose of the well within the monitoring program and will range from monthly to seasonal, coinciding with the existing monitoring program.

The extended list is to be repeated at least every other year. Certain parameters such as volatile organics may be required more frequently.

Routine sampling should occur seasonally, as described earlier in this appendix. In addition to the three routine monitoring periods yearly, an annual report is due in January which describes the monitoring results for the previous year. See Section 10 of this manual for more information on contents of the annual report.

Parameters required for routine monitoring include, at a minimum:

Ammonia Nitrogen
Chemical Oxygen Demand
Chloride
Iron, Dissolved
Nitrate + Nitrite, as N
pH(1)
Specific Conductance(2)
Sulfate
Temperature(2)
Water Elevation(3)

(1) Two measurements: in field, immediately after obtaining sample and in laboratory.
(2) As measured in field.
(3) As measured in field before pumping or bailing.

All samples should be obtained following methodology and analytic techniques of this manual.

Routine monitoring should continue for five years after the site is closed, whereupon the monitoring program will be reevaluated by the Agency. Recommendations will be made to either increase or decrease monitoring requirements. Following the initial post-closure reevaluation, monitoring should continue as directed by the Agency for a period of 15 additional years (20 total years post-closure). If no contamination is detected during this period, monitoring may cease at the site. All wells should be abandoned in accordance with the Minnesota Water Well Construction Code when monitoring ceases. NOTE: Post-closure requirements may change when the rules regulating solid waste disposal are changed in 1985.

INDUSTRIAL WASTE LANDFILLS

The monitoring requirements for industrial waste landfills will be determined on a case-by-case basis by the Agency based upon such factors as:

1. Site characteristics,
2. Waste reactivity, and
3. Present and potential downgradient water uses.

DEMOLITION WASTE LANDFILLS

Monitoring will be required at demolition landfills on a case-by-case basis, depending on the waste type, site size, operational history, and controls on dumping. If required to monitor, the guidelines for sanitary landfills should be followed.

RAPID INFILTRATION BASINS

In some cases, municipal wastewater which has received at least primary treatment may be discharged to rapid infiltration basins. The nature of these systems is such that ground water impacts may be significant, and therefore monitoring is required.

Monitoring systems should be designed to provide the information necessary to effectively evaluate any impacts which the system may exert upon the ground water. For more information on the design of monitoring systems to meet Agency requirements, see "Guidelines for Ground Water Monitoring System Design" (MPCA, 1985). A sufficient number of piezometers are also necessary to assess the dimensions (height and areal extent) of the ground water mound. Water elevations should be monitored during loading events to assess the dimensions of the ground water mound and allow for operational modifications to the system, if necessary. Water quality testing may be required as frequently as monthly. Samples should be obtained following the procedures given in this manual. Parameters to be analyzed can include:

Alkalinity
Ammonia Nitrogen
Chemical Oxygen Demand
Chloride
Nitrate + Nitrite, as N
pH(1)
Specific Designation of Basins Loaded
Specific Conductance(2)
Temperature(2)
Volatile Organics(3)
Water Elevation(4)

(1) Two measurements: in field, immediately after obtaining sample and in laboratory.
(2) As measured in field.
(3) Halogenated and non-halogenated, purge-and-trap method.
(4) As measured in field before pumping or bailing.

Analyses should be performed in accordance with the requirements of this manual, pages 26-30.

Monitoring should continue for at least one year after site closure, when the Agency will evaluate the need for continued monitoring. All wells should be abandoned in accordance with the Minnesota Water Well Construction Code when monitoring ceases.

SPILLS

Monitoring may be required at spill sites if the material spilled is hazardous, if seepage into ground water is suspected, or if a potential exists for negative impacts on water supplies. In these instances, the need for continuing monitoring will be evaluated on a case-by-case basis, following review of site-specific hydrogeologic information.

SURFACE IMPOUNDMENTS

Currently, all agricultural, municipal, and industrial ponds which are required to have National Pollutant Discharge Elimination System or State Disposal System permits and which seep, as evidenced by relatively small or no surface discharges must perform a water balance study. Also, a water balance must be conducted on newly-constructed ponds to verify that construction criteria have been met. Instructions for conducting a water balance study are given in the Agency document "Design/Operability Handbook," currently in draft form.

A ground water impact study is required when the water balance study indicates seepage in excess of 3500 gallons per acre per day if the system was approved prior to May 16, 1975. Monitoring may also be required at sites which have less than 3500 gallons per acre per day based on pollution potential from that particular site. Facilities approved after that date will be individually reviewed to determine the appropriate action.

Monitoring wells should be installed around the perimeter of the stabilization pond system and downgradient from each pond. A sufficient number of wells should be installed to determine background water quality. In addition, the approximate area downgradient that could potentially be affected by seepage must be established.

Samples should be obtained from the wells following methods and analytical techniques of this manual.

Initial sampling should occur at least monthly for a three-month period. Routine monitoring is then conducted on a quarterly basis, if required. For municipal and agricultural impoundments, the parameters to be analyzed include:

Alkalinity
Ammonia Nitrogen
Chemical Oxygen Demand
Chloride
Fecal Coliform
Hardness
Nitrate + Nitrite, as N
pH[(1)]
Sodium
Specific Conductance[(2)]
Sulfate
Temperature[(2)]
Total Kjeldahl Nitrogen
Total Phosphorus
Water Elevation[(3)]

(1) Two measurements: in field, immediately after obtaining sample and in laboratory.
(2) As measured in field.
(3) As measured in field before pumping or bailing.

Waste-specific parameters should be included in the monitoring of industrial impoundments. The Agency will review the data and determine appropriate follow-up action. Often, this action may involve upgrading the pond seal so that it meets the standard for new ponds.

Table A-2

Summary of Monitoring Parameters

	Solid Waste Landfill Routine Monitoring	Solid Waste Landfill Extended Monitoring	Community Drainfield	Land Application Site	Rapid Infiltration Basin	Surface Impoundment (Wastewater)
Alkalinity		X	X		X	X
Arsenic, Dissolved		X				
Cadmium, Dissolved		X				
Calcium, Dissolved		X				
Chemical Oxygen Demand	X	X	X		X	X
Chloride	X	X	X	X	X	X
Chromium, Dissolved		X				
Copper, Dissolved		X				
Fecal Coliforms			X		X	X
Hardness			X		X	X
Influent Flow			X		X	X
Inspection Pipe Observation			X			
Iron, Dissolved	X	X				
Lead, Dissolved		X				
Magnesium, Dissolved		X				
Manganese, Dissolved		X				
Mercury, Dissolved		X				
Nitrogen, Ammonia	X	X	X	X	X	X
Nitrogen, Kjeldahl			X		X	X
Nitrogen, Nitrate + Nitrite	X	X	X	X	X	X
pH	X	X	X	X	X	X
Phosphorus, Total						X
Potassium, Dissolved		X				
Sodium, Dissolved		X				X
Solids, Total Dissolved		X				
Solids, Total Suspended		X				
Specific Area of Application			X	X	X	
Specific Conductance	X	X	X	X	X	X
Sulfate	X	X	X		X	X
Temperature	X	X	X		X	X
Volatile Organics		X	X		X	
Zinc, Dissolved		X				
Water Elevations	X	X	X	X	X	X

APPENDIX B:

USE OF THE VANDORN AND KEMMERER SAMPLERS

(Excerpted from "Quality Control Manual"
an in-house Minnesota Pollution Control Agency document)

VANDORN SAMPLER

The VanDorn sampler is designed for use in the deep waters of oceans and lakes. The Minnesota Pollution Control Agency (MPCA) uses two types of VanDorn samplers: 1) the vertical model, and 2) the horizontal model. The vertical model is used for standard sampling while the horizontal model is used for sampling near the bottom and thermoclines. The VanDorn samplers used by the MPCA are all made of plastic. They are cylindrical in shape and have capacities of 2.2, 4.2 and 30.2 liters. All models have a drain on the bottom for drawing off samples.

Through the middle of the VanDorn sampler there is a flexible rubber tube which is connected to the two end stoppers. The end stoppers have a trip wire on each stopper. The trip wire hooks onto the trip mechanism. The sounding line is attached to the trip mechanism.

The VanDorn sampler should be cleaned and then wiped dry before storage. To prevent damage to the sampler a wooden case is provided for transport and storage. The rubber tube used to close the end stoppers should be replaced yearly.

To set the sampler, pull one of the end stoppers out and attach the trigger wire to the trigger mechanism. Repeat this step with second stopper. Slowly lower sampler down to the desired sampling depth. Send down the messenger to trip the trigger mechanism. Bring the sampler to the surface. Problems may be incurred during rough water conditions which may cause drifting of the boat and subsequent failure of the tripping mechanism due to non-vertical profile of sounding line.

It is advisable before actual sampling to make sure the sampler works properly. Make sure to use a flat-nosed brass messenger, 11 ounces or smaller and a 3/16" or 1/4" braided nylon line attached securely to the sampler. Use of any other messenger or line may result in damage or loss of the sampler. If possible sampler should be allowed to soak in the lake or stream to be sampled for at least 15 minutes prior to sampling and kept in the sample water or kept closed between sample stations.

KEMMERER SAMPLER

The Kemmerer sampler is a basic water or wastewater sampler. It is designed to collect samples at specific depths.

The Kemmerer is a long cylindrical tube constructed of metal or plastic with rubber stoppers at each end. The stoppers and an associated mechanical device enables the operator to lower the open sampler to a pre-determined depth, close the sampler, and retrieve a sample from that depth.

The metal samplers are usually used for collection of samples for the common physical, and chemical determinations including pesticides. The plastic models, while satisfactory for the foregoing parameters except pesticides, are usually used for collection of samples for trace metals. The Minnesota Pollution Control Agency (MPCA) has Kemmerer samplers of 1.2, 3.1, and 6.1 liter capacities.

Whenever possible, the Kemmerer should be transported in the case that is provided, and care should be taken during handling to avoid damage. The Kemmeer should be cleaned thoroughly, then wiped down with a clean cloth before storage.

The Kemmerer sampler is used as follows:

1. Pull open the top stopper (this will also lock open the bottom stopper).

2. Rinse sampler with distilled water or in the water to be sampled before lowering the device.

3. Lower the sampler to the desired depth and close the sampler by dropping the messenger down the line.

4. Retrieve the sampler and empty contents into sampler container.

Before sampling it is important to make sure the line is tied securely to the sampler, and that the other end of the line is fastened to guard against loss of the sampler. It is good practice to take a trial sample before actual sampling starts to make sure the sampler works properly. When sampling for trace metals the plastic Kemmerer should be used, and it should be washed down with de-ionized water before each use. A 3/16" or 1/4" braided nylon sound line should be used with a flat-nosed 11 ounce or smaller messenger. Use of any other lines of messengers may result in damage or loss of the equipment.

APPENDIX C:

RECOMMENDATION FOR SAMPLE CONTAINERS
AND PRESERVATION OF SAMPLES

from: "Handbook for Sampling and Sample Preservation of Water and Wastewater" U.S. Environmental Protection Agency EPA-600/4-82-029, September 1982

NOTE: These recommendations have not yet been formally adopted by the U.S. Environmental Protection Agency

CONTAINERS, PRESERVATION TECHNIQUES, AND HOLDING TIMES

Parameter	Container[1]	Preservative[2, 12]	Maximum Holding Time[3]
Bacterial Tests			
Coliform, fecal and total	P,G	Cool, 4°C 0.008% $Na_2S_2O_3$[6]	6 hours
Fecal streptococci	P,G	Cool, 4°C 0.008% $Na_2S_2O_3$[6]	6 hours
Inorganic Tests			
Acidity	P,G	Cool, 4°C	14 days
Alkalinity	P,G	Cool, 4°C	14 days
Ammonia	P,G	Cool, 4°C H_2SO_4 to pH < 2	28 days
Biochemical oxygen demand	P,G	Cool, 4°C	48 hours
Biochemical oxygen demand, carbonaceous	P,G	Cool, 4°C	48 hours
Bromide	P,G	None required	28 days
Chemical oxygen demand	P,G	H_2SO_4 to pH < 2	28 days
Chloride	P,G	None required	28 days
Chlorine, total residual	P,G	None required	Analyze immediately
Color	P,G	Cool, 4°C	48 hours
Cyanide, total and amenable to chlorination	P,G	Cool, 4°C NaOH to pH > 12 0.6 g ascorbic acid[6]	14 days[9]
Fluoride	P	None required	28 days
Hardness	P,G	HNO_3 to pH < 2	6 months
Hydrogen ion (pH)	P,G	None required	Analyze immediately
Kjeldahl and organic Nitrogen	P,G	Cool, 4°C H_2SO_4 to pH < 2	28 days

Parameter	Container[1]	Preservative[2, 12]	Maximum Holding Time[3]
Metals[4]			
Chromium VI	P,G	Cool, 4°C	24 hours
Mercury	P,G	HNO_3 to pH < 2	28 days
Metals, except above	P,G	HNO_3 to pH < 2	6 months
Nitrate	P,G	Cool, 4°C	48 hours
Nitrate-nitrite	P,G	Cool, 4°C H_2SO_4 to pH < 2	28 days
Nitrite	P,G	Cool, 4°C	48 hours
Oil and grease	G	Cool, 4°C H_2SO_4 to pH < 2	28 days
Organic carbon	P,G	Cool, 4°C HCl or H_2SO_4 to pH < 2	28 days
Orthophosphate	P,G	Filter immediately Cool, 4°C	48 hours
Oxygen, Dissolved Probe	G bottle and top	None required	Analyze immediately
Winkler	G bottle and top	Fix on site and store in dark	8 hours
Phenols	G only	Cool, 4°C H_2SO_4 to pH < 2	28 days
Phosphorus (elemental)	G	Cool, 4°C	48 hours
Phosphorous, total	P,G	Cool, 4°C H_2SO_4 to pH < 2	28 days
Residue, total	P,G	Cool, 4°C	7 days
Residue, Filterable	P,G	Cool, 4°C	7 days
Residue, Non-filterable (TSS)	P,G	Cool, 4°C	7 days
Residue, settleable	P,G	Cool, 4°C	48 hours
Residue, volatile	P,G	Cool, 4°C	7 days

Parameter	Container[1]	Preservative[2, 12]	Maximum Holding Time[3]
Silica	P	Cool, 4°C	28 days
Specific conductance	P,G	Cool, 4°C	28 days
Sulfate	P,G	Cool, 4°C	28 days
Sulfide	P,G	Cool, 4°C, add zinc acetate plus sodium hydroxide to pH > 9	7 days
Sulfite	P,G	Cool, 4°C	Analyze immediately
Surfactants	P,G	Cool, 4°C	48 hours
Temperature	P,G	None required	Analyze immediately
Turbidity	P,G	Cool, 4°C	48 hours
Organic Tests[5]			
Purgeable halocarbons	G, Teflon-lined septum	Cool, 4°C 0.008% $Na_2S_2O_3$[6]	14 days
Purgeable aromatics	G, Teflon-lined septum	Cool, 4°C 0.008% $Na_2S_2O_3$[6] HCl to pH < 2[10]	14 days
Acrolein and acrylonitrile	G, Teflon-lined septum	Cool, 4°C 0.008% $Na_2S_2O_3$[6] Adjust pH to 4-5[11]	14 days
Phenols	G, Teflon-lined septum	Cool, 4°C 0.008% $Na_2S_2O_3$[6]	7 days until extraction, 40 days after extraction
Benzidines	G, Teflon-lined septum	Cool, 4°C 0.008%$Na_2S_2O_3$[6]	7 days until extraction, 40 days after extraction

Parameter	Container[1]	Preservative[2, 12]	Maximum Holding Time[3]
Phthalate esters	G, Teflon-lined cap	Cool, 4°C	7 days until extraction, 40 days after extraction
Nitrosamines[7]	G, Teflon-lined cap	Cool, 4°C store in dark $0.008\% Na_2S_2O_3$[5]	7 days until extraction, 40 days after extraction
PCB's	G, Teflon-lined cap	Cool, 4°C pH 5-9	7 days until extraction, 40 days after extraction
Nitroaromatics and isophorone	G, Teflon-lined cap	Cool, 4°C	7 days until extraction, 40 days after extraction
Polynuclear aromatic hydrocarbons	G, Teflon-lined cap	Cool, 4°C $0.008\% Na_2S_2O_3$[6] store in dark	7 days until extraction, 40 days after extraction
Haloethers	G, Teflon-lined cap	Cool, 4°C $0.008\% Na_2S_2O_3$[5]	7 days until extraction, 40 days after extraction
Chlorinated hydrocarbons	G, Teflon-lined cap	Cool, 4°C	7 days until extraction, 40 days after extraction
TCDD	G, Teflon-lined cap	Cool, 4°C $0.008\% Na_2S_2O_3$[6]	7 days until extraction, 40 days after extraction
Pesticides Tests			
Pesticides	G, Teflon-lined septum	Cool, 4°C pH 5-9[8]	7 days until extraction, 40 days after extraction
Radiological Tests			
Alpha, beta and radium	P,G	HNO_3 to pH < 2	6 months

1. Polyethylene (P) or Glass (G).

2. Sample preservation should be performed immediately upon sample collection. For composite samples, each aliquot should be preserved at the time of collection. When use of an automated sampler makes it impossible to preserve each aliquot, then samples may be preserved by maintaining at 4°C until compositing and sample splitting is completed.

3. Samples should be analyzed as soon as possible after collection. The times listed are the maximum times that samples may be held before analysis and still considered valid. Samples may be held for longer periods only if the permittee, or monitoring laboratory, has data on file to show that the specific types of samples under study are stable for the longer time. Some samples may not be stable for the maximum time period given in the table. A permittee, or monitoring laboratory, is obligated to hold the sample for a shorter time if knowledge exists to show this is necessary to maintain sample stability.

4. Samples should be filtered immediately on-site before adding preservative for dissolved metals.

5. Guidance applies to samples to be analyzed by GC, LC, OR GC/MS for specific compounds.

6. Should only be used in the presence of residual chlorine.

7. For the analysis of diphenylnitrosamine, add 0.008% $Na_2S_2O_3$[6] and adjust pH to 7-10 with NaOH within 24 hours of sampling.

8. The pH adjustment may be performed upon receipt at the laboratory and may be omitted if the samples are extracted with 72 hours of collection. For the analysis of aldrin, add 0.008% $Na_2S_2O_3$.

9. Maximum holding time is 24 hours when sulfide is present.

10. Sample receiving no pH adjustment must be analyzed within seven days of sampling.

11. Samples for acrolein receiving no pH adjustment must be analyzed within three days of sampling.

12. When any sample is to be shipped by common carrier or sent through the United States Mails, it must comply with the Department of Transportation Hazardous Materials Regulations (49 CFR Part 172). The person offering such material for transportation is responsible for ensuring such compliance. For the preservation requirements of this section, the Office of Hazardous Materials, Materials Transportation Bureau, Department of Transportation has determined that the Hazardous Materials Regulations do not apply to the following materials: Hydrochloric acid (HCl) in water solutions at concentrations of 0.04% by weight or less (pH about 1.96 or greater); Nitric acid (HNO_3) in water solutions at concentrations of 0.15% by weight or less (pH about 1.62 or greater); Sulfuric acid (H_2SO_4) in water solutions at concentrations of 0.35% by weight or less (pH about 1.15 or greater); and Sodium hydroxide (NaOH) in water solutions at concentrations of 0.080% by weight or less (pH about 12.30 or less).

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DIRECTIONS FOR REVISION TO QAPP APPENDIX B

1. Remove entire Appendix B and discard

2. Insert:

   - Appendix B cover sheet

   - Appendix B Index of Standard Operating Procedures

   - LM-RMA-3024 - Determination of Low Level (Part per trillion) PAH and Heterocycles in Water

   - LM-RMA-1112 - Total Recoverable Phenolics - City of St. Louis Park

APPENDIX B

STANDARD OPERATING PROCEDURES

REVISED
Oct., 1990

INDEX OF STANDARD OPERATING PROCEDURES

Title: DETERMINATION OF LOW LEVEL (PART PER TRILLION) PAH AND HETEROCYCLES IN WATER - LM-RMA-3024

1.0 Summary of the Method

This method has been designed for the analysis of polynuclear aromatic hydrocarbons (PAH) and heterocyclic compounds at the part per trillion level (ppt,ng/L) in water. The analysis is carried out by isolation of the target analytes by liquid-liquid extraction of the water sample with an organic solvent. Quantitation of the isolated target analytes is performed by gas chromatography mass spectrometry (GC/MS) in the selected ion monitoring mode (SIM). The compounds listed in Table 1 can be quantitatively determined using this analytical method.

This method has two options for the extraction of the samples depending on the sample type. The two options include a low and medium level extraction. The low level option has typical reporting limits of 10.0 ppt. The medium level option is eighty times higher in detection limits. A volume of sample dependent of the extraction option chosen is extracted with methylene chloride. Analysis of concentrated extract is performed by gas chromatography/mass spectrometry using the selected ion monitoring scanning mode under electron impact ionization conditions.

2.0 Interferences

Method interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing hardware that lead to discrete artifacts and/or elevated baselines in the ion current profiles. All of these materials must be routinely demonstrated to be free from interferences under the conditions of the analysis by running laboratory reagent blanks.

Matrix interferences may be caused by contaminants that are coextracted from the sample. The extent of matrix interferences will vary considerably from source to source, depending upon the nature of the environment being sampled.

An interference which is unique to selecting ion monitoring techiques can arise from the presence of an interfering compound which contains the quantitation mass ion. This event results in a positive interference to the reported value for the compound of interest. This interference is controlled to some degree by acquiring data for a confirmation ion. If the ion ratios between the quantitation ion and the confirmation ion are not the specified limits, then interferences may be present.

3.0 Apparatus and Materials

3.1 Glassware

Glassware must be scrupulously cleaned. Clean all glassware as soon as possible after use by rinsing with the last solvent used in it. This should be followed by detergent washing with hot water, and rinses with tap water, reagent water, then methanol.

Glassware should then be oven dried at 150°C for 30 minutes, and heated in a muffle furnace at 400°C for 15 to 30 minutes. Solvent rinses with benzene and methylene chloride may be substituted for the muffle furnace heating. Volumetric glassware should not be heated in a muffle furnace. After drying and cooling, glassware should be sealed and stored in a clean environment to prevent any accumulation of dust or other contaminants.

Store glassware inverted or capped with aluminum foil. The use of high purity reagents and solvents helps to minimize interference problems. Purification of solvents by distillation in all-glass systems may be required.

3.1.1 Separatory funnel - 2000 and 4000 ml, with Teflon stopcock or continuous liquid liquid extractor, 2000 mL.

3.1.2 Drying column - glass funnel with ~10 cm anhydrous sodium sulfate.

3.1.3 Concentrator tube, Kuderna-Danish - 10 mL, graduated (Kontes K-570050-1025 or equivalent). Calibration must be checked at the volumes employed in the test. Ground-glass stoppers are used to prevent evaporation of extracts.

3.1.4 Snyder column, Kuderna-Danish - Three-ball macro (Kontes K-503000-0121 or equivalent).

3.1.5 Evaporative flask, Kuderna-Danish - 500 mL (Kontes K-570001-0500 or equivalent). Attach to concentrator tube with springs or clips.

3.1.6 Nitrogen evaporation device equipped with a water bath that can be maintained at 35-40°C. The N-Evap by Organomation Associates, Inc., South Berlin, MA (or equivalent) is suitable.

3.1.7 Micro reaction vessels, 2.0 mL (Supelco 3-3295).

3.2 Gas Chromatograph

The analytical system includes a temperature programmable gas chromatograph and all required accessories including syringes, analytical columns, and gases. The injection port is designed for on-column injection when using packed columns and for spitless injection when using capillary columns.

3.3 Column

A Quadrex 25 meter fused silica capillary column coated with DB5 bonded phase, or equivalent.

3.4 Mass Spectrometer

A mass spectrometer operating at 70 ev (nominal) electron energy in the electron impact ionization mode and tuned to maximize the sensitivity of the instrument to the compounds being analyzed. The GC capillary column is fed directly into the ion source of the mass spectrometer.

A computer system interfaced to the mass spectrometer allows the continuous acquisition and storage on machine-readable media of all mass spectra obtained throughout the duration of the chromatographic program. The computer has software that allows searching any GC/MS data file for ions of a specific mass and plotting such ion abundances versus time or scan number. The computer allows acquisition at pre-selected mass windows for selected ion monitoring.

4.0 Reagents

4.1 Reagent water

Reagent water is defined as water in which the target compounds are not observed at or above the method detection limit.

4.2 Solvents

Acetone, methanol, methylene chloride, cyclohexane - Burdick & Jackson, distilled in glass, or equivalent.

4.3 Sodium sulfate

(ACS) Granular, anhydrous. Purify by heating at 400^{0}C for 4 hours in a shallow tray.

4.4 Surrogate Spiking Solution

Depending on the extraction option chosen low or medium a surrogate solution is made by weighing an appropriate aliquot of each purified crystal into a volumetric flask and diluting to volume with methanol or acetone and added to the sample prior to extraction in methylene chloride. The compounds in the surrogate solutions are naphthalene-d8, fluorene-d10, and chrysene-d12. The low surrogate solution is at 10 ng/ml and 0.5 ml per liter of sample is added. The medium surrogate solution is at 1000 ng/ml and 1.0 ml is added to the 500 ml sample.

4.5 Internal Standard Solutions

A solution containing ca. 400 ng/mL of each internal standard is prepared by weighing an appropriate aliquot of each purified crystal into a volumetric flask and diluting to volume with methylene chloride. Fifty microliters of this solution is added to the 0.5 ml extract prior to analysis to give a concentration of the internal standards in the extract of 40 ng/mL.

4.6 Matrix Recovery Standard Spiking Solution

A solution containing the following compounds at the listed concentrations is prepared by weighing an appropriate aliquot of each purified crystal into a volumetric flask and diluting to volume with methanol or acetone. The concentrations of the spiking solution for both the low and medium level extractions are shown below:

Compound	Low Spiking Solution Concentration (ng/ml)	Medium Spiking Solution Concentration (ng/ml)
Naphthalene	20	2000
Fluorene	20	2000
Chrysene	20	2000
Indene	20	2000
Quinoline	20	2000
Benzo(e)pyrene	20	2000
2-methyl naphthalene	20	2000

The low spiking solution at 0.5 ml per liter of sample. The medium level spiking solution is added at 1.0 ml per 500 ml of sample.

5.0 Sample Preservation, Storage and Holding Times

5.1 Sample Preservation and Storage

The samples must be protected from light and refrigerated at 4°C ($\pm$ 2°C) from the time of receipt until extraction and analysis. After analysis, extracts and unused sample volume must be protected from light and refrigerated at 4°C ($\pm$ 2°C).

5.2 Holding Times

Samples must be extracted within 5 days of the time of sample receipt. Samples are required to be shipped the same day samples are collected using an overnight carrier.

Extracts must be analyzed within 40 days of extraction.

6.0 Sample Extraction

6.1 Samples

Samples are extracted at a ph>12. For the low level extraction, a measured amount of sample, approximately 4 liters, is separated into two 2-liter aliquots and poured into either two 2-liter continuous liquid-liquid extractors or two 4 liter separatory funnels. The surrogate solution is added and they are extracted with methylene chloride. The samples are shaken three times with 80 mL of methylene chloride for the shakeout technique. The samples are allowed to reflux for eighteen hours if the liquid-liquid extractor technique is used for preparation. The extracts from each two-liter fractional extraction (for either technique) are then combined for concentration. The medium level extraction requires that 500 mL of the sample be extracted with methylene chloride for 18 hours in a one liter continuous liquid-liquid extractor or shaken three times with 60 mLs of methylene chloride in a 2-liter separatory funnel. The extracts are passed through an anhydrous sodium sulfate drying column into a 500 mL Kuderna-Danish evaporative concentrator.

The low level extract is concentrated to approximately 0.5 mL and transferred to a 2.0 mL microreaction vessel. The methylene chloride is evaporated using a nitrogen stream. The evaporative concentrator tube is successively rinsed with methylene chloride, the rinsings added to the reaction vessel and the methylene chloride again evaporated. This process is continued until at least five (5) 1 mL rinsings of the tube have occurred.

The final methylene chloride extract for the low level extraction is evaporated to 500 ul. All microreaction vessels are permanently marked at the 500 ul level and additional methylene chloride added, when necessary, to insure a final 500 ul extract volume. The medium level extract is concentrated to 5.0 ml using the same procedure described above. The extract vessels are capped with a Teflon fitted septum cap and stored at 4°C prior to GC/MS analysis.

6.2 Method blank

Method blanks are prepared by treating a 4-L or 500 ml of laboratory reagent water exactly as described above depending on the option chosen. A method blank must be performed once each case*, each 14 calendar day period during which samples in a case are received, with every 20 samples of similar concentration and/or sample matrix or whenever samples are extracted by the same procedure, whichever is most frequent.

* A case is a group or a set of samples collected from a particular site over a given period of time.

6.3 Matrix Recovery Sample

Matrix recovery samples are prepared by spiking a sample as described in section 4.6. The fortified sample is extracted exactly as described above for samples. The laboratory will spike and analyze 5% matrix spike samples (i.e. one matrix spike with every 20 samples).

6.4 Duplicate Sample

For a minimum of 10% of the samples analyzed a duplicate sample will be taken at sampling and a duplicate analysis will be performed. This will be carried out to insure that an estimate of precision will be available.

7.0 GC/MS Calibrations

Prior to use of the method for low level analysis of PAH, a five-point response factor calibration curve must be established showing the linear range of analysis. Only one level of calibration is used for low level and medium low level ppt PAH analysis. The concentrations of standards used to construct the calibration curve are 20, 40, 240, 1200, and 4800 ng/mL. The linear range for low level analysis (4 L to 0.5 mL) corresponds to sample concentrations of 2.5, 5, 30, 150, and 600 ng/L. If the concentration of any target compound in a sample exceeds the linear range defined by the above standards, the extracts must be diluted so that the concentrations of all target compounds fall within the range of the calibration curve. The linear range for medium low level analysis (0.5 L to 5.0 mL) corresponds to final sample concentrations of 200, 400, 2400, 12000, and 48000 ng/L. For every 12 hours of GC/MS analysis, the mass spectrometer response for each PAH relative to the internal standard is determined, as described in the Calculations section, using daily check standards at concentrations of 40 ng/mL. Daily response factors for each compound must be compared to the initial calibration curve. If the daily response factors are within ±30 percent of the corresponding calibration curve value the analysis may proceed. If, for any analyte, the daily response factor is not within ±30 percent of the corresponding calibration curve value, a five-point calibration curve must be repeated for that compound prior to the analysis of samples.

Table 2 contains example RRT data for target compounds.

8.0 Daily GC/MS Performance Tests

The GC/MS will not be tuned to meet decafluorotriphenylphosphine (DFTPP) ion abundance criteria. EPA has dropped this requirement for selected ion monitoring (SIM) methods. This allows the laboratory to tune the instrument to maximize the sensitivity for the compounds being analyzed as described below.

Mass tuning will be performed using the mass calibration compound FC43. Tuning will be performed to maximize the sensitivity of the mass spectrometer for the mass range of compounds being analyzed. In the FC43 spectra, the ion abundance of masses 131 and 219 are adjusted to a approximate ratio of 1:1. These two ions are then maximized to be approximately 50 to 70% of the ion abundance of the base mass 69. This procedure maximizes the sensitivity of the instrument in the mass region of interest for the PAH analysis.

9.0 Gas Chromatography/Mass Spectrometry Analysis

Just prior to analysis an aliquot of internal standard solution is transferred to the sample vial using a 250 uL syringe to give a final internal standard concentration of 40 ng/mL in the extract. Representative aliquots are injected into the capillary column of the gas chromatograph using the following, or similar conditions:

Injector Temp - 250°C
Transfer Line Temp - 290°C
Initial Oven Temp - 30°C
Initial Hold Time - 1 min.
Ramp Rate - 10°C/min.
Final Temperature - 325°C

The effluent from the GC capillary column is fed directly into the ion source of the mass spectrometer. The MS is operated in the selected ion monitoring (SIM) mode using appropriate windows to include the quantitation and confirmation masses for each PAH as shown in Table 1. For all compounds detected at a concentration above the MDL, a check is made to insure the confirmation ion is present.

10.0 Calculations

10.1 Qualitative Identification

Obtain EICPs for the primary m/z and the confirmatory ion. The following criteria must be met to make a qualitative identification:

The characteristic masses of each parameter of interest must maximize in the same or within one scan of each other.

For the qualitative identification, the relative retention time (RRT) of unknown peaks fall within +/- 0.06 RRT units.

The relative peak heights of the primary ion compared to the confirmation or secondary ion masses in the EICPs must fall within $\pm$ 20% of the relative intensities of these masses in a reference mass spectrum. The reference mass spectrum can be obtained from a standard analyzed in the GC/MS system or from a reference library. In some instances a compound that does not meet secondary ion confirmation criteria may still be determined to be present in a sample after close inspection of the data by the mass spectroscopist. Supportive data includes the presents of the secondary ion but the ratio is greater than $\pm$ 20% of the primary ion which may be caused by an interference of the secondary ion. When the primary ion is not affected by interferences and the decision is agreed to by the reviewer, the compound is flagged with an asterisk (*) on the sample summary sheet.

Structural isomers that have very similar mass spectra and less than 30 s difference in retention time, can be explicitly identified only if the resolution between authentic isomers in a standard mix is acceptable. Acceptable resolution is achieved if the baseline to valley height between the isomers is less than 25% of the sum of the two peak heights. Otherwise, structural isomers are identified as isomeric pairs.

10.2 Quantitation

The following formula is used to calculate the response factors of the internal standard to each of the calibration standards.

$$RF = (A_s C_{is})/(A_{is} C_s)$$

where:

A_s = Area of the characteristic ion for the parameter to be measured.
A_{is} = Area of the characteristic ion for the internal standard.
C_{is} = Concentration of the internal standard, (ng/mL).
C_s = Concentration of the parameter to be measured, (ng/mL).

Based on these response factors, sample extract concentrations for each PAH is calculated using the following formula.

$$Ce = \frac{(A_s)(I_s)}{(A_{is})(RF)}$$

where:

Ce = Sample extract concentration (ng/mL)
A_s = Area of the characteristic ion for the parameter to be measured.
A_{is} = Area of the characteristic ion for the internal standard.
I_s = Amount of internal standard added to each extract (ng/mL).

The actual sample concentration (C) for each compound is calculated by the following formula:

$$C = (Ce) \times \frac{V_E}{V_s},$$

C = Concentration in Sample (ng/L)
V_E = The final extract volume (mL), and
V_s = The original volume of sample extracted (L).

11.0 Quality Control/Quality Assurance

11.1 GC/MS Tuning

The GC/MS is tuned as described in section 8.0.

11.2 GC/MS Initial Calibration and Continuing Calibration Check

Prior to the use of the method for low level analysis of PAH, a five-point response factor calibration curve must be established showing the linear range of the analysis.

Each calibration standard is analyzed and the area of the primary characteristic ion is tabulated against concentration for each compound. The response factor (RF) for each compound at each concentration level is calculated using the following equation:

$$RF = \frac{A_s}{A_{is}} \times \frac{C_{is}}{C_s}$$

A_s = Area of the characteristic ion for the compound to be measured.
A_{is} = Area of the characteristic ion for the specific internal standard.
C_{is} = Concentration of the internal standard
C_s = Concentration of the compound to be measured.

For every 12 hours of GC/MS analysis, the mass spectrometer response (RF) for each PAH of interest (Table 1) relative to the internal standard is determined.

These daily response factors for each compound must be compared to the initial calibration curve. The percent difference is calculated using the following equation:

$$\% \text{ Difference} = \frac{\overline{RFI} - RFC}{\overline{RFI}} \text{ X } 100$$

$\overline{RFI}$ = Average response factor from initial calibration.

RFC = Response factor from current verification check standard.

If the daily response factor are within ± 35 percent of the corresponding calibration curve value the analysis may proceed. If, for any analyte, the daily response factor is not within ± 35 percent of the corresponding calibration curve value, a five-point calibration curve must be repeated for that compound prior to the analysis of samples.

11.3 Method Blank Analysis

A method blank consists of deionized, distilled laboratory water carried through the entire analytical scheme (extraction, concentration, and analysis). The method blank volume must be approximately equal to the sample volumes being processed.

Method blank analysis are performed at the rate of one per case*, each 14 calendar day period during which samples in a case are received, with every 20 samples of similar concentration and/or sample matrix, or whenever samples are extracted by the same procedure, whichever is most frequent.

If the method blank contains any of the carcinogenic PAHs listed in table 10-3 at concentrations greater than the method detection limit (MDL), or any other target PAH compound at a concentration 5 times greater than the MDL, the method blank will be considered out of control. Corrective action will include reanalysis of the blank extract, an investigation into laboratory sources of contamination and qualifying that sample data relates to the blank. Blank level contamination should be considered the minimum level of contamination in all samples that are analyzed with the blanks.

* A case is a group or a set of samples collected from a particular site over a given period of time.

11.4 Surrogate Compound Analysis

The laboratory will spike all samples and quality control samples with deuterated PAH surrogate compounds. The surrogate compounds will be spiked into the sample prior to extraction and this will measure individual sample matrix effects associated with sample preparation and analysis. They will include naphthalene-d_8, fluorene-d_{10}, and chrysene-d_{12}.

RMAL will take corrective action whenever the surrogate recovery for any one or more surrogates is outside the following acceptance criteria:

Surrogate	Acceptance Criteria % Low-Level
Naphthalene-d8	14-108
Fluorene-d10	41-162
Chrysene-d12	10-118

The following corrective action will be taken when required as stated above:

a) Check calculations to assure there are no errors;

b) Check internal standard and surrogate solutions for degradation, contamination, etc., and check instrument performance;

c) If the surrogate recovery is outside the control limits, the secondary ion may be used to check the quantitation of the surrogate. If the secondary ion meets within the control limits this recovery is reported with flag of # next to the percent recovery.

d) If the upper control limit is exceeded for only one surrogate, and the instrument calibration, surrogate standard concentration, etc. are in control, it can be concluded that an interference specific to the surrogate was present that resulted in high recovery and this interference would not affect the quantitation of other target compounds. The presence of this type of interference can be confirmed by evaluating the chromatographic peak shapes in ion intensities of the surrogate.

e) If the surrogate could not be measured because the sample required a dilution, no corrective action is required. The recovery of the surrogate is recorded as D with the note surrogate diluted out.

f) Reanalyze the sample or extract if the steps above fail to reveal a problem. If reanalysis of the extract yields surrogate recoveries within the stated limits, then the reanalysis data will be used. Both the original and reanalysis data will be reported.

11.5 Matrix Spike Analysis

The laboratory will spike and analyze 5% matrix spike samples. RMAL will spike seven representative compounds into water. These compounds and the spiking levels as listed in section 4.4. The initial matrix spike criteria for data validity are as follows:

o The average of the percent recoveries for all seven compounds must fall between 20 and 150 percent.

o Only one compound can be below its required minimum percent recovery. These minimum percent recoveries are:

1) 10% for chrysene and benz(e)pyrene

2) 20% for all other compounds.

Criteria for data validity for each individual matrix spike compound will be developed as data is collected and will be updated on a quarterly basis.

If the matrix spike criteria are not met, the matrix spike analysis will be repeated. If the subsequent matrix spike analysis meets the criteria, then the reanalysis data will be used. If not, the data for the sample will be reported but qualified as being outside the acceptance criteria of the method. Both the original and reanalysis data will be reported.

11.6 Duplicates

The laboratory will analyze 10% duplicate samples. Percent difference between duplicates will be calculated for each detected compound. Corrective action will be performed if the relative difference is greater than 70% for target compounds.

TABLE 1

COMPOUNDS AND MS QUANTITATION MASS IONS*

Compound	Quantitation Mass Ion	Confirmation Ion	Internal Standard Reference
Polynuclear Aromatic Hydrocarbons (PAH)			
Naphthalene	128	102	1
Acenaphthylene	152	151	1
Acenaphthene	154	153	1
Fluorene	166	165	1
Phenanthrene	178	176	2
Anthracene	178	176	2
Fluoranthene	202	200	2
Pyrene	202	200	2
Benzo(a)anthracene	228	226	3
Chrysene	228	226	3
Benzofluoranthenes	252	250	3
Benzo(a)pyrene	252	250	3
Indeno(1,2,3,cd)pyrene	276	274	3
Dibenz(a,h)anthracene	278	279	3
Benzo(g,h,i)perylene	276	274	3
Internal Standards			
1) Acenaphthene-d10	164		--
2) Phenanthrene-d10	188		--
3) Benzo(a)pyrene-d12	264		--
Surrogates			
1) Naphthalene-d8	136	134	1
2) Fluorene-d10	176	174	1
3) Chrysene-d12	240	236	3

*** The relative peak heights of the primary ion compared to the confirmation or secondary ion masses in the EICP's must fall within +/- 20% of the relative intensities of these masses in a reference mass spectrum.**

Title: DETERMINATION OF LOW LEVEL (PART PER TRILLION) PAH AND HETEROCYCLES IN WATER - LM-RMA-3024

TABLE 1

COMPOUNDS AND MS QUANTITATION MASS IONS

Compound	Quantitation Mass Ion	Confirmation Ion	Internal Standard Reference
Polynuclear Aromatic Hydrocarbons (PAH)			
Naphthalene	128	102	1
Acenaphthylene	152	151	1
Acenaphthene	154	153	1
Fluorene	166	165	1
Phenanthrene	178	176	2
Anthracene	178	176	2
Fluoranthene	202	200	2
Pyrene	202	200	2
Benzo(a)anthracene	228	226	3
Chrysene	228	226	3
Benzofluoranthenes	252	250	3
Benzo(a)pyrene	252	250	3
Indeno(1,2,3,cd)pyrene	276	274	3
Dibenz(a,h)anthracene	278	279	3
Benzo(g,h,i)perylene	276	274	3
Internal Standards			
1) Acenaphthene-d10	164		--
2) Phenanthrene-d10	188		--
3) Benzo(a)pyrene-d12	264		--
Surrogates			
1) Naphthalene-d8	136	134	1
2) Fluorene-d10	176	174	1
3) Chrysene-d12	240	236	3

TABLE 1 (Continued)

Compound	Quantitation Mass Ion	Confirmation Ion	Internal Standard Reference
Heterocycles and Other PAH			
Indene	116	115	1
Indole	117	90	1
2,3-dihydroindene	117	118	1
2,3-benzofuran	118	90	1
Quinoline	129	102	1
Benzo(b)thiophene	134	89	1
2-methylnaphthalene	141	115	1
1-methylnaphthalene	141	115	1
Biphenyl	154	153	1
Carbazole	167	166	2
Dibenzofuran	168	139	1
Acridine	179	178	2
Dibenzothiophene	184	139	2
Perylene	252	250	3
Benzo(e)pyrene	252	250	3
Internal Standards			
1) Acenaphthene-d10	164		--
2) Phenanthrene-d10	188		--
3) Benzo(a)pyrene-d12	264		--
Surrogates			
1) Naphthalene-d8	136	134	1
2) Fluorene-d10	176	174	2
3) Chrysene-d12	240	236	3

TABLE 2

RELATIVE RETENTION TIMES AND CONFIDENCE FOR THE COMPOUNDS
ASSOCIATED WITH THE LOW LEVEL PAH AND HETEROCYCLE METHODOLOGY

	Absolute Retention Time (minutes)	Avg. RRT	SD	% RSD	95% Confidence Limits
Benzofuran	8:03	0.550	0.015	2.807	0.520-0.580
Dihydroindene	8:45	0.590	0.016	2.765	0.558-0.622
Indene	8:54	0.598	0.016	2.699	0.566-0.630
Naphthalene-d8(Surr.)	11:14	0.733	0.017	2.289	0.699-0.767
Naphthalene	11:16	0.735	0.017	2.289	0.701-0.769
Benzo(b)thiophene	11:25	0.743	0.017	2.258	0.709-0.777
Quinoline	12:06	0.783	0.017	2.140	0.749-0.817
Indole	12:55	0.824	0.018	2.167	0.788-0.860
2-methylnaphthalene	12:59	0.832	0.017	2.084	0.798-0.866
1-methylnaphthalene	13:15	0.848	0.017	2.055	0.814-0.882
Biphenyl	14:12	0.901	0.017	1.921	0.867-0.935
Acenaphthylene	15:15	0.962	0.018	1.822	0.927-0.988
Acenaphthene	15:44	0.988	0.018	1.849	0.952-1.024
Dibenzofuran	16:09	1.011	0.018	1.791	0.975-1.047
Fluorene-d10(Surr.)	16:57	0.872	0.015	1.735	0.842-0.902
Fluorene	17:01	0.875	0.015	1.745	0.845-0.905
Dibenzothiophene	19:08	0.974	0.016	1.617	0.942-1.006
Phenanthrene	19:28	0.988	0.016	1.589	0.956-1.020
Anthracene	19:34	0.994	0.016	1.597	0.962-1.026
Acridine	19:42	0.999	0.016	1.572	0.967-1.031
Carbazole	20:02	1.013	0.015	1.487	0.983-1.043
Fluoranthene	22:32	1.130	0.017	1.461	1.096-1.164
Pyrene	23:07	1.157	0.017	1.443	1.123-1.191
Benz(a)anthracene	26:16	0.873	0.012	1.325	0.849-0.897
Chrysene-d12 (Surr.)	26:18	0.874	0.012	1.320	0.850-0.898
Chrysene	26:22	0.876	0.012	1.320	0.852-0.900
Benzofluoranthenes	29:00	0.960	0.014	1.501	0.932-0.988
Benzo(e)pyrene	29:34	0.984	0.016	1.590	0.952-1.016
Benzo(a)pyrene	29:44	0.988	0.016	1.615	0.956-1.020
Perylene	29:55	0.996	0.016	1.644	0.964-1.028
Indeno(1,2,3 cd)pyrene	32:31	1.114	0.025	2.276	1.064-1.164
Dibenz(ah)anthracene	32:36	1.113	0.031	2.743	1.051-1.175
Benzo(ghi)perylene	33:17	1.149	0.028	2.422	1.093-1.205

TABLE 3

SELECTED ION MONITORING (SIM) SEQUENCES FOR PAH AND HETEROCYCLES

Sequence #	M/Z Scanned	Scan # Range	Start Time (min)
1	90,115,116,117,118	0 - 399	0:00
2	90,115,116,117,118	400 - 849	4:40
3	89,102,128,129,134,136	850 - 1064	9:55
4	90,115,117,141	1065 - 1169	12:26
5	151,152,153,154,164	1170 - 1354	13:39
6	139,165,166,168,176	1355 - 1524	15:49
7	139,176,178,179,184,188	1525 - 1684	17:48
8	166,167	1685 - 1799	19:40
9	200,202,226,228,240	1800 - 2299	21:00
10	241,250,252,256	2300 - 2479	26:50
11	250,252,264,268	2480 - 2649	28:56
12	274,276,278,279,302,303	2650 - 3500	30:55

Title: DETERMINATION OF LOW LEVEL (PART PER TRILLION) PAH AND HETEROCYCLES IN WATER - LM-RMA-3024

TABLE 4
LOW LEVEL PNA SPIKE RESULTS

Compound	Conc. ng/L	Percent Recovery
2,3-Benzofuran #	4.3	86
2,3-Dihydroindene	4.7	94
1H-Indene #	4.3	87
Naphthalene	5.9	118
Benzo(B)thiophene #	3.8	76
Quinoline	5.9	118
1H-Indole #	4.7	94
2-Methylnaphthalene	5.0	101
1-Methylnaphthalene	4.4	87
Biphenyl	4.2	83
Acenaphthylene	4.1	82
Acenaphthene	4.4	88
Dibenzofuran	4.0	81
Fluorene	4.5	89
Dibenzothiophene #	4.2	85
Phenanthrene	5.3	105
Anthracene	4.4	89
Acridine	5.4	107
Carbazole	5.2	104
Fluoranthene	5.0	101
Pyrene	5.1	102
Benzo(A)anthracene	4.1	82
Chrysene	4.2	83
Benzo(B)fluoranthrene	4.0	80
Benzo(K)fluoranthrene	4.8	97
7,12-Dimethylbenzanthracene #	3.5	70
Benzo(E)pyrene	4.0	80
Benzo(A)pyrene	4.7	95
Perylene	4.0	80
3-Methylcholanthrene	4.0	81
Indeno(1,2,3-CD)pyrene	4.4	88
Dibenz(A,C)anthracene	4.5	90
Dibenz(A,H)anthracene	4.7	93
Benzo(G,H,I)perylene	4.9	98
Naphthalene-d8 *	---	72
Fluorene-d10 *	---	84
Chrysene-d12 *	---	74

Note: All compounds spiked at 5 ng/L.
Qualitative confirmation ion greater than +-20% of reference spectrum.
* Surrogate compound.

STANDARD
OPERATING
PROCEDURE

Subject or Title: Total Recoverable Phenolics - City of St. Louis Park (Manual)		Page 1 of 16
SOP No.: LM-RMA-1112	Revision No.: 1.0	Effective Date: June 13, 1990
Supersedes: Original		

1. Scope and Application

   1.1 This method measures steam-distillable phenolic materials which react with the color reagents under the conditions of the analysis.

   1.2 The detection limit is 5 ug/L as Phenol.

   1.3 This method is applicable to the analysis of drinking, surface and saline waters, domestic and industrial wastes, and soil samples.

   1.4 The range extends to 0.1 mg/L. The range can be extended by dilution of the samples.

   1.5 Approximate preparation time is 2 hours for a group of 10 samples. Analytical time is about 15 minutes per sample.

2. Summary of Method

   The sample is acidified and distilled to separate phenolics from interfering compounds. Phenolics in the distillate react with 4-aminoantipyrene in the presence of potassium ferricyanide at pH 10 to form a reddish-brown dye, which is extracted into chloroform and measured colorimetrically at 460 nm.

3. Comments

   3.1 Interferences

      3.1.1 Most direct interferences are eliminated by distillation of an acidified sample. Phenolic compounds distill with the water but interfering compounds do not.

Prepared by: Lindsay Breyer	Date: June 13, 1990
Management Approval: Anne Lang	Date: June 14, 1990
QA Officer Approval: Jean Zimmerman	Date: June 15, 1990

3.1.2 Some phenolic compounds are not steam-distillable and will not be determined.

3.1.3 The colors produced by various phenolic compounds are not the same, so the response will depend on the compounds actually present in the samples. Phenol has been selected as the calibration standard since it is not possible to reproduce the mixture of compounds present in the sample. The result obtained will represent the minimum concentration of phenolics present in the sample.

3.1.4 Interference from sulfur compounds is eliminated by acidification and addition of copper sulfate.

3.1.5 Oxidizing agents such as chlorine will oxidize phenolic compounds and must be removed.

3.1.6 Oil may distill over and interfere with the analysis.

3.1.7 Aromatic amines may react with nitrite (if present) to produce phenolic compounds.

4. Safety Issues

4.1 All employees are expected to be familiar with and follow the procedures outlined in the Enseco/RMAL safety plan. Lab coats and safety glasses are required in all laboratory areas at all times. If you have any questions or safety concerns, see your supervisor or safety officer.

4.2 Wear gloves and apron when handling concentrated acids, bases and solvents. Transport only in approved carriers. Avoid breathing fumes and vapors; handle in a fume hood. Neutralize and clean up any spills immediately. In case of skin contact, flush affected area with water for at least 15 minutes. Notify your supervisor or safety officer of any spills or exposures.

4.3 Wear gloves, apron, and face shield when performing distillations. Distillations are to be performed under the slot hood.

4.4 Phenol is extremely toxic and can be absorbed through the skin. Handle only in a fume hood and wear gloves. In case of skin contact, flush with water for at least 15 minutes. Notify your supervisor or safety officer of any exposures.

4.5 Extractions are to be performed in a fume hood. Wear gloves and apron. Take care to keep chloroform vapors confined to the hood.

4.6 Samples, reagents and other solutions containing high concentrations of toxic materials must not be flushed down the sinks, but are to be disposed of in suitable waste containers.

5. Samples Collection and Preservation

5.1 Samples are to be collected in glass containers and preserved by adding sulfuric acid to pH < 2 and refrigerating at 4°C.

5.2 The holding time is 28 days.

6. Apparatus

6.1 All-glass distillation apparatus consisting of 500 mL round-bottom flask with side arm, coil condenser, heating mantle with controller, and associated adapters and hardware.

6.2 Recirculating chiller.

6.3 pH meter and electrode.

6.4 Separatory funnels, 500 mL, with supporting rack.

6.5 Porcelain spot-test plate.

6.6 Spectrophotometer with 2 cm cells.

6.7 Filter funnels.

6.8 Filter paper, Whatman 41.

6.9 Micropipettes with disposable tips, 10 uL, 20 uL, 1 mL.

6.10 Miscellaneous laboratory apparatus and glassware.

7. Reagents and Standards

7.1 Sulfuric Acid, 50%

Slowly add 500 mL concentrated sulfuric acid to 500 mL deionized water with constant mixing and cool. The reaction is very exothermic and should be done with extreme caution.

7.2 Boiling stones.

7.3 Copper Sulfate, 10%

Dissolve 100 g cupric sulfate 5-hydrate in deionized water and dilute to 1000 mL.

7.4 Ferrous Ammonium Sulfate Solution

Add 1 mL concentrated sulfuric acid to 500 mL deionized water. Add 1.1 g ferrous ammonium sulfate, mix until dissolved, and dilute to 1000 mL.

7.5 Buffer Solution

Dissolve 16.9 g ammonium chloride in 143 mL concentrated ammonium hydroxide and dilute to 250 mL with deionized water. Prepare this solution in a hood. Two milliliters of this solution should adjust the pH of 100 mL distillate to 10.

7.6 Aminoantipyrene Solution

Dissolve 2.0 g of 4-aminoantipyrene in deionized water and dilute to 100 mL.

7.7 Potassium Ferricyanide Solution

Dissolve 8 g potassium ferricyanide in deionized water and dilute to 100 mL.

7.8 Phenol Stock Standard, 1000 mg/L

Dissolve 1.000 g phenol in deionized water and dilute to 1000 mL.

7.9 Phenol Intermediate Standard, 1.0 mg/L

Dilute 1.0 mL 1000 mg/L Stock Standard to 1000 mL with deionized water.

7.10 Working Standards

Dilute the 1.0 mg/L Intermediate Standard with deionized water as follows:

Aliquot (mL)	Final Vol. (mL)	Conc. (mg/L)
0	200	Blank
1.0	200	0.005
2.0	200	0.010
4.0	200	0.020
10.0	200	0.050
20.0	200	0.100

Note: The standards are not distilled with the samples.

7.11 pH test strips

7.12 Starch/iodide test strips

7.13 Lead Acetate test strips

8. Procedure

8.1 Sample Preparation

8.1.1 Measure and record the pH of all water samples. pH test strips may be used.

8.1.2 Check for residual chlorine with starch/iodide test strips. A blue to black color indicates a positive test. Record the result on the bench sheet.

8.1.3 Check for sulfide using lead acetate test strips. A dark color indicates the presence of sulfide. Record the result on the bench sheet.

8.1.4 Measure 200 mL sample into a distillation flask and add a few boiling stones. For soil and waste samples, use 2.0 g and add 200 mL deionized water. Be sure to adjust the pH of soil and waste samples before distillation. Record the exact weight on the bench sheet.

8.1.5 If the chlorine test was positive, add ferrous ammonium sulfate solution until a negative test is obtained.

8.1.6 If the pH is not < 2, add 50% sulfuric acid dropwise until it is.

8.1.7 If the sulfide test was positive, add 2 mL 10% copper sulfate.

8.1.8 Assemble the distillation apparatus, turn on the cooling water and hood, and start the distillation. Capture the distillate in a 250 mL beaker.

8.1.9 When 150 to 175 mL distillate has been collected, turn off the heating mantle and allow to cool.

8.1.10 Add 25 to 30 mL deionized water and resume distillation until 200 mL has been collected. Turn off the heating mantle and clean out the flask when cool. Do not over distill the samples as this will lead to interferences in the analysis.

8.1.11 Transfer the distillates to 250 mL glass bottles with teflon caps and refrigerate until the are analyzed.

8.2 Spot Test

8.2.1 Place 1 mL aliquots of each sample in the wells of a porcelain spot test plate. Also run a blank (deionized water) and the 0.10 mg/L standard.

8.2.2 Add 20 uL buffer solution to each well and stir.

8.2.3 Add 10 uL aminoantipyrene solution and stir.

8.2.4 Add 10 uL potassium ferricyanide solution and stir.

8.2.5 Compare the color of the samples to the color of the blank and standard. Any samples appearing darker than the standard will require dilution prior to analysis. Make note of these on the bench sheet along with the estimated dilution required. If necessary, dilute the sample and spot check the dilution.

8.3 Dilution Technique

8.3.1 Since the sample volumes may not be exactly 200 mL after distillation, it is not possible to make dilutions volumetrically. Dilutions must be done on a weight basis.

8.3.2 Place a beaker on a top loading balance and zero it.

8.3.3 Pour the entire sample into the beaker and note the weight.

8.3.4 Divide the weight by the required dilution factor to determine the sample weight to be analyzed. For example, if there are 205 g distillate and a 10x dilution is needed, 20.5 g of the distillate should be analyzed.

8.3.5 Measure out this weight of sample for analysis and dilute to a total volume of 200 mL. Return the unused portion of the sample to the original container. Record all dilutions made on the bench sheet.

8.4 Analysis of Samples

8.4.1 Place 200 mL sample (or standard) in a 500 mL separatory funnel. Analysis should be performed in a hood.

8.4.2 Add 4 mL buffer solution and mix.

8.4.3 Check the pH with a pH meter (pH paper is not sensitive enough). The pH should be 10 $\pm$ 0.2. If necessary, adjust the pH by dropwise addition of ammonium hydroxide or hydrochloric acid.

8.4.4 Add 2 mL aminoantipyrene solution and mix.

8.4.5 Add 2 mL potassium ferricyanide and mix.

8.4.6 Wait 3 minutes, then add 25 mL chloroform.

8.4.7 Shake the separatory funnel 10 times. Vent chloroform fumes into the hood. Then allow the phases to separate.

8.4.8 Shake the funnel another 10 times and let the chloroform settle.

8.4.9 Filter the chloroform extracts through filter paper into 2 cm cuvettes.

8.4.10 Measure and record the absorbances at 460 nm, zeroing on chloroform; not the blank.

8.4.11 If any samples measure higher than the highest standard, up to a 5x dilution may be made on the extract with chloroform. Record the dilution on the bench sheet and make it clear that the chloroform extract was diluted, as the calculation will be affected.

9. QA/QC Requirements

9.1 QC Samples

9.1.1 A blank (deionized water) is required with every batch of 20 less samples. The blank must be taken through the entire prep and analysis with the samples. Additional blanks, termed "Initial Calibration blank" (ICB) and "Continuing Calibration Blank" (CCB) are also analyzed. These blanks are used only to evaluate the determinative step and are not distilled. They are analyzed at a frequency of one ICB per 20 samples and one CCB per 10 samples.

9.1.2 The calibration is verified by the analysis of two different laboratory check standards. An "Initial Calibration Verification" (ICV) check standard is analyzed at a frequency of one per 20 samples. This check is carried through the entire procedure, including the distillation step. The measured value from this check standard must be between 75% and 125% of the true value.

A "Continuing Calibration Verification" (CCV) check standard is analyzed at a frequency of one per 10 samples. This standard is used to verify the determinative step only. The measured value must be between 85% and 115% of the true value.

If the measured values from the check standards are not within control limits, the system is out of control and corrective action must be performed.

9.1.3 Save the original blank and standards; new ones do not have to be extracted.

9.1.4 Duplicate analyses are performed at a frequency of 5%. Corrective action is performed if the relative difference from the duplicate analysis is greater than 70%.

9.1.5 Matrix spikes will be performed at a frequency of 5%. The spike level is 50 ug/L. The recovery of the matrix spike must be between 75% and 125%. Corrective action is performed if these criteria are not achieved.

9.2 Acceptance Criteria

9.2.1 An acceptable blank must not contain phenolics above the nominal reporting limit of 5 ug/L. If any of the blanks contain phenolics above 5 ug/L, the system is out of control and corrective action must be performed.

9.2.2 ICV and CCV recoveries must be 75 - 125%.

9.2.3 Matrix spike recoveries must be between 75% and 125%.

9.2.4 The calibration curve must have a correlation coefficient of at least 0.995.

9.3 Corrective Action Required

9.3.1 The color reaction is very sensitive to pH and the extraction technique. Check the pH of all samples before developing the color. Use the same extraction technique for all samples and standards.

10. Calculations

10.1 Subtract the blank absorbance from the standard and sample absorbances. If the chloroform extract was diluted, divide the blank absorbance by the dilution factor before subtracting.

10.2 Enter the corrected standard readings into a linear least squares program to determine the calibration curve.

10.3 Calculate the sample results from their corrected absorbances using the least squares program. Multiply by any dilutions made during prep or analysis.

11. Data Reporting Deliverables

The data packages for total phenolics shall as closely follow CLP deliverables for inorganic analysis as possible. Reports shall contain all applicable CLP forms as well as the associated raw analytical data. The package includes Forms I - III, V and VI (results, initial and continuing calibration verification, blanks, matrix spike and duplicate). Examples of these forms are included in this SOP (Pages 11-16). The report shall be organized as described in CLP SOW 7/88.

SOP No.:	Revision No.:	Effective Date:
LM-RMA-1112	1.0	June 13, 1990

12. References

12.1 Method source: EPA Methods 420.1, 420.2

12.2 Deviations from source method and rationale

12.2.1 There is a discrepancy between the preservation methods and holding times given in the method and those given in the table of containers and preservatives at the front the methods book. We have chosen to use sulfuric acid to adjust the sample pH to 2 since this has been done traditionally at RMAL.

12.2.2 The size of the distillation apparatus and volumes of sample and reagent were reduced to conserve space and speed up the analysis.

12.2.3 Provisions have been made for dilution of the chloroform extracts up to 5x. This is sometimes necessary for samples which are overrange and cannot be reprepped due to limited sample volume or other reasons.

COVER PAGE - INORGANIC ANALYSES DATA PACKAGE

Lab Name: ROCKY MOUNTAIN ANALYTICAL Contract: \ Project: \

Lab Code: ENSECO Case No.: \ SAS No.: \ SDG No.: \

SOW No. 7/88

RMA Sample No.	Client Sample ID.
\	\
\	\
\	\
\	\
\	\
\	\
\	\
\	\
\	\
\	\

PARAMETERS	METHOD	DETECTION LIMIT	SOURCE
Phenolics	420.1	5 ug/L	1

COMMENTS:

\
\

SOURCE:
1="Methods for Chemical Analysis of Water and Wastes," USEPA-EMSL, Cincinnati.

I certify that this data package is in compliance with the terms and conditions of the contract, both technically and for completeness, for other than the conditions detailed above. Release of the data contained in this hardcopy data package has been authorized by the Laboratory Manager or the Manager's designee, as verified by the following signature.

Signature: ____________________ Name: ____________________

Date: ____________________ Title: ____________________

1
INORGANIC ANALYSIS DATA SHEET

Lab Name: ROCKY MOUNTAIN ANALYTICAL   Contract: \

Lab Code: ENSECO   Case No.: \   SAS No.: \

Matrix (soil/water): \   SDG No.: \

Level (low/medium): \

% Solids: \

RMA Sample No.
\
Client Sample ID.
\

Project: \

Date Received: \

Concentration Units (ug/L or mg/kg dry weight): \

Analyte	Concentration	C	Q	M
Phenolics				

Color Before: \   Clarity Before: \   Texture: \

Color After: \   Clarity After: \   Artifacts: \

Comments:

\
\

FORM I - IN

7/88

2A
INITIAL AND CONTINUING CALIBRATION VERIFICATION

Lab Name: ROCKY MOUNTAIN ANALYTICAL Contract: \

Lab Code: ENSECO Case No.: \ SAS No. \ SDG No.: \

Initial Calibration Source: \

Continuing Calibration Source: \

Concentration Units: ug/L

	Initial Calibration			Continuing Calibration					
Analyte	True	Found	%R(1)	True	Found	%R (1)	Found	%R (1)	M
Phenolics									

SOP No.: LM-RMA-1112	Revision No.: 1.0	Effective Date: June 13, 1990

3
BLANKS

Lab Name: ROCKY MOUNTAIN ANALYTICAL Contract: \

Lab Code: ENSECO Case No.: \ SAS No.: \ SDG No.: \

Preparation Blank Matrix (soil/water): \

Preparation Blank Concentration Units (ug/L or mg/kg): \

Analyte	Initial Calib. Blank (ug/L)	C	Continuing Calibration Blank (ug/L) 1	C	2	C	3	C	Preparation Blank	C	M
Phenolics											

5A
SPIKE SAMPLE RECOVERY

RMA Sample No.
\
Client Sample ID.
\

Lab Name: ROCKY MOUNTAIN ANALYTICAL Contract: \

Lab Code: ENSECO Case No.: \ SAS No.: \ SDG No.: \

Matrix: \ Level (low/medium): \

% Solids for Sample: \

Concentration Units (ug/L or mg/kg dry weight): \

Analyte	Control Limit % R	Spiked Sample Result (SSA)	C	Sample Result (SA)	C	Spike Added (SA)	% R	Q	M
Phenolics									

Comments: \

FORM V (Part 1) - IN

7/88

6
DUPLICATES

RMA Sample No.
\
Client Sample ID.
\

Lab Name: ROCKY MOUNTAIN ANALYTICAL   Contract: \

Lab Code: ENSECO   Case No.: \   SAS No.: \   SDG No.: \

Matrix (soil/water): \   Level (low/medium): \

% Solids for Sample: \   % Solids for Duplicate: \

Concentration Units (ug/L or mg/kg dry weight): \

Analyte	Control Limit	Sample (S)	C	Duplicate (D	C	RPD	Q	M
Phenolics								

FORM VI - IN

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